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Watershed Manipulation Project: Quality Assurance
Implementation Plan for 1986-1989

NSI Technology Services Corp., Corvallis, OR

Prepared for:

Corvallis Environmental Research Lab., OR

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**WATERSHED MANIPULATION PROJECT:
QUALITY ASSURANCE IMPLEMENTATION PLAN FOR 1986-1989**

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ABSTRACT

The Watershed Manipulation Project (WMP) was implemented by EPA to:

1. Identify and quantify the relative importance of various processes in controlling surface water acidification with particular emphasis on the role of sulfate adsorption and base cation supply in the long-term watershed response to acidic deposition;
2. Assess the quantitative and qualitative watershed response to various levels of acidic deposition; and
3. Evaluate the assumptions that underlie the Direct/Delayed Response Project (DDRP) models and their ability to predict short-term watershed responses to experimental manipulation.

These objectives will be achieved through a series of experiments at various spatial and temporal scales ranging from laboratory, plot, hillslope, and catchment manipulations.

A number of hypotheses have been formulated both at the process level and the catchment level to achieve the WMP objectives. This document describes the quality assurance and quality control (QA/QC) program implemented by WMP for measurements made during the first three years of the project. Companion documents describe the field procedures implemented during that time, and the rationale for the WMP hypotheses. Future documents will document QA/QC and field procedures for the final three years of the project.

PREFACE

The purpose of Quality Assurance/Quality Control (QA/QC) is to ensure that data from research and monitoring studies are of known and documented quality to satisfy project objectives. QA/QC is an integral and important part of all of the U.S. Environmental Protection Agency's (EPA) Aquatic Effects Research Program (AERP) projects. The Watershed Manipulation Project (WMP) is a research project designed to: assess the quantitative and qualitative response of watershed soil and surface waters to altered deposition, determine the interactions among biogeochemical mechanisms controlling surface water response to acidic deposition, and test the behavior of the AERP Direct/Delayed Response Project (DDRP) watershed models. The WMP is designed to test specific hypotheses relating various watershed process responses to acidic deposition at a variety of temporal and spatial scales through an interdisciplinary research approach. To ensure the data from various laboratory, plot, hillslope and catchment studies will satisfy the WMP objectives, a QA Plan is required that integrates QA/QC activities across all these studies. This document describes the integrated approach to QA/QC for the WMP, and is intended to supplement the WMP Field Implementation Plan, FY87-89 (Erickson et al., 1990) and provide QA/QC guidance for all personnel associated with the WMP. As a dynamic and evolving document, the QA Plan will be updated and revised with growth and change within the WMP.

This is the second version of the original WMP Integrated QA Plan and is intended to reflect what quality assurance procedures were implemented during the first three years of program operation. The original WMP Integrated QA Plan was released May 1987 prior to finalization of sampling and experimental designs at the Bear Brook Watersheds in Maine (BBWM), and contained protocols and experimental approaches that have since been modified as the project direction evolved. All implemented quality assurance activities were approved and monitored by EPA staff.

This plan replaces the first release of the WMP Integrated QA Plan. This version is an official EPA document and should be referenced for all activities covering the first three years of the project. A new QA plan covering the second three years of project operation is in preparation.

Contributions from research cooperators are gratefully acknowledged. Amy Vickland (NSI) provided important editorial assistance. A special thanks goes to Carol Roberts (NSI) for her patient typing of all drafts of this manuscript.

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SECTION 1

INTRODUCTION

QUALITY ASSURANCE

The purpose of the U.S. Environmental Protection Agency's (EPA) Quality Assurance (QA) Program is to ensure that environmentally related data used in research and monitoring projects are of known and documented quality to satisfy project objectives. Differing methodologies, lack of data comparability, unknown data quality, and poor coordination of sampling and analysis efforts are problems that can be minimized if QA is an integral part of the research design. This document discusses the QA Plan for the EPA Watershed Manipulation Project (WMP) and describes the integration of QA throughout the WMP.

The QA Plan for the WMP represents a dynamic document. Because of the program duration, changes have been and may continue to be incorporated to reflect amended protocols and/or research approaches. In addition, the overall approach of assessing data quality may be revised as experience is gained through implementation of the QA Plan. Changes can be made in either of two ways: through a formal annual review by program participants and on an as-needed basis in the event that problems or improvements are identified. Approval of all revisions will be obtained from EPA Project and QA officers.

QUALITY ASSURANCE REQUIREMENTS

EPA policy requires each office or laboratory generating data to implement minimum procedures to assure that precision, accuracy, completeness, comparability, and representativeness of data are known and documented (QAMS, 1980). Each office or laboratory is required to specify the quality levels that data must meet to be acceptable and satisfy project objectives. This requirement applies to all environmental monitoring and measurement efforts mandated or supported by EPA through regulations, grants, contracts, or other formal agreements. To ensure that this responsibility is met uniformly across EPA, each organization must have a written QA Project Plan covering each monitoring or measurement activity within a project.

QA activities are, however, far more than requirements or the simple monitoring of the quality of the data being generated in a research project. QA activities can be used as tools to help project participants decide where to put energy and resources to improve the quality of research being conducted. A QA Project Plan specifically presents the policies, organization, objectives, functional activities, QA and quality control (QC) activities to achieve the data quality objectives (DQOs) of the project and to help map out future research directions that should be taken.

QUALITY ASSURANCE ELEMENTS

EPA requires that 16 elements be discussed in a QA Project Plan. These 16 elements and where they are located in this document are listed in Table 1. The remainder of this document describes and discusses the integrated QA Plan for the WMP. QA plans for specific "Tasks" within WMP are included as appendices.

TABLE 1. ESSENTIAL ELEMENTS OF A QA PLAN LISTED IN THIS WMP QA PLAN

Element	Section No.	Task Plan Appendices Section No.
1. Title Page	p. i	p. 1
2. Table of Contents	p. vi	p. 2
3. Project Description	2	1.0
4. Project Organization and Responsibility	2	2.0
5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability	3	3.0
6. Sampling Procedures	6	4.0
7. Sample Custody	6	5.0
8. Calibration Procedures and Frequency	6	7.0
9. Analytical Procedures	6	6.0
10. Data Reduction, Validation and Reporting	2,6	11.0
11. Internal Quality Control Checks	4,6	9.0
12. Performance and System Audits	5,6	10.0
13. Preventative Maintenance	6	8.0
14. Specific Routine Procedures Used to Assess Data Precision, Accuracy and Completeness	3,4,6	9.0
15. Corrective Action	4,6	9.0
16. Quality Assurance Reports to Management	7	12.0

SECTION 2

PROJECT DESCRIPTION AND ORGANIZATION

PROJECT DESCRIPTION

Watershed Manipulation Project Objectives

The EPA's Environmental Research Laboratory-Corvallis (ERL-C) initiated the WMP as part of the EPA Aquatic Effects Research Program (AERP). The WMP's field activities are conducted at the Bear Brook watershed in Maine (BBWM), located in southeastern Maine.

The objectives of the WMP are to:

- Assess the quantitative and qualitative response of watershed soil and surface waters to altered deposition;
- Determine the interactions among biogeochemical mechanisms controlling surface water response to acidic deposition; and
- Test the behavior of the EPA's Direct/Delayed Response Project (DDRP) watershed models (MAGIC, ILWAS, ETD) and evaluate model predictions of manipulation outcomes.

Watershed Manipulation Project Hypotheses

The DDRP model structures and process formulations function as a frame to identify and evaluate process interactions and watershed responses to acidic deposition. Hypotheses related to surface water acidification are integrated in the three dynamic watershed models used in the DDRP. These hypotheses have been formally identified in the WMP and stated, in general, for processes relating to:

- Hydrology
- Cation Release
 - Mineral Weathering
 - Ion Exchange
 - Aluminum
- Mobile Anions
 - Sulfur
 - Nitrogen
 - Organic Acids

Each of the hypotheses, its specific relation to the model structure assumed in DDRP, and its specific experimental design are described and discussed in Appendix C of the QA Plan, the WMP, Rationale for Hypothesis Formulation and Testing document (Thornton and Wigington, 1990), and the WMP Field Implementation Plan, FY87-90 (Erickson et al., 1990).

PROJECT ORGANIZATION AND RESPONSIBILITY

Project Organization

The organizational structure is designed to promote close cooperation, collaboration, and communication among individuals participating in the WMP. The WMP organizational structure integrates the Site and Task Teams with the EPA Management Team, a Modeling Support Group, a Review Committee and a Watershed Oversight Committee (Figure 1). The organizational structure is designed to maximize the interaction among Site and Task Leaders. Support for data management, QA/QC and general administration is provided through EPA. The independent Modeling Support Group provides general modeling support for the Site and Task Leaders. The Review Committee provides a review of research plans and proposals and participates in overall project reviews. The Watershed Oversight Committee periodically reviews progress and the proposed research direction. This highly interactive structure requires that QA/QC procedures associated with each Site and Task study be integrated to ensure data transferred or exchanged among studies is of sufficient and known quality to satisfy the study's objectives and requirements.

Project Responsibilities

The Site Team, Task Groups, and EPA Management Team have the primary responsibility for field and laboratory experiments, and associated QA/QC. The key personnel associated with the entire WMP are listed in Table 2.

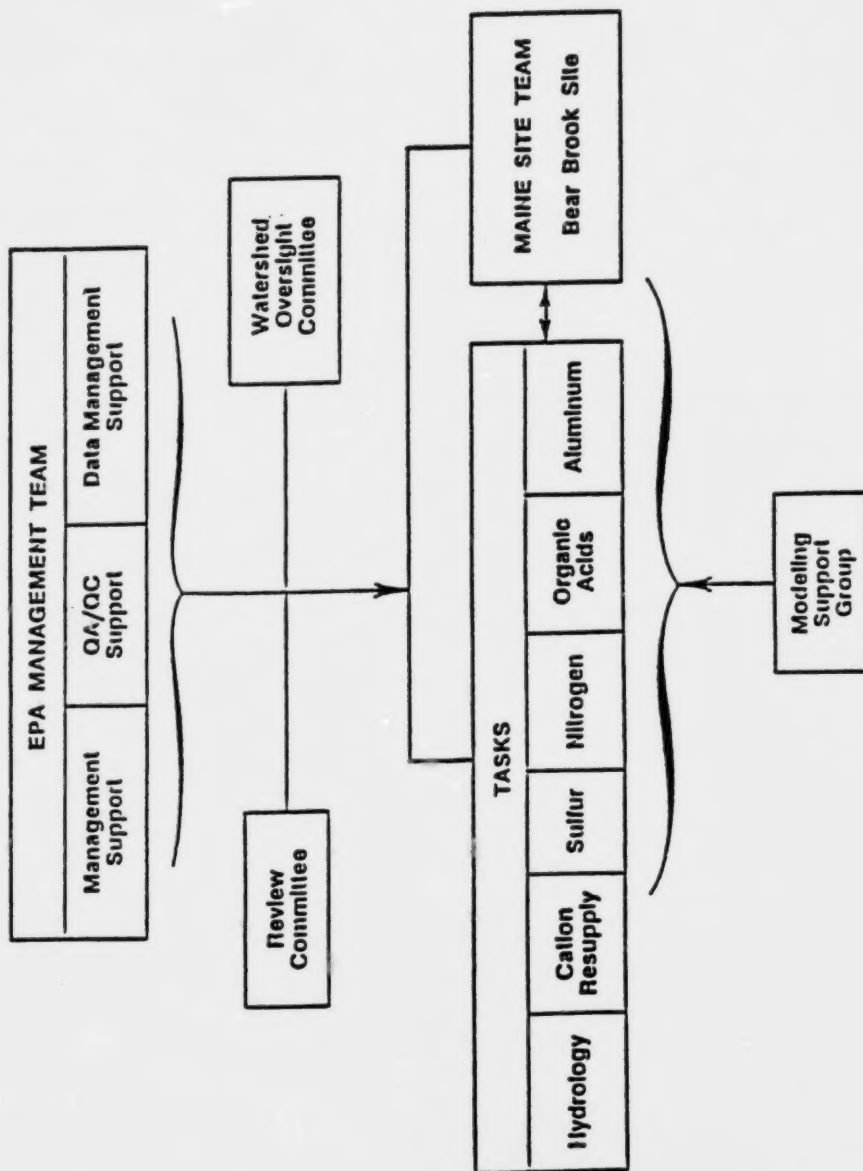


Figure 1. Watershed Manipulation Project Organizational Structure.

TABLE 2. KEY PERSONNEL (1986-1989)

o Maine Site Team
(University of Maine)

Stephen A. Norton
Ivan J. Fernandez
Terry A. Haines
Stephen C. Nodvin
Jeffrey S. Kahl
Lindsey E. Rustad
John P. Scofield
Anne M. Narahara

o Tasks:

- Hydrologic Pathways
(University of Virginia)
(Rutgers University)
(University of Lancaster)

George M. Hornberger, Leader
Peter F. Germann
Keith Bevin

- Aluminum and Base Cation Release
(Syracuse University)
(State Univ. of NY (SUNY)-Plattsburg)
(Syracuse University)

Charles T. Driscoll, Leader
Robert D. Fuller
Drew C. McAvoy

- Cation Resupply and Chemical Weathering
(University of Iowa)
(University of Wyoming)
(University of Iowa)

Jerald L. Schnoor, Leader
James I. Drever
Richard T. Valentine

- Nitrate Mobility and Nitrogen Cycling
(University of New Hampshire)
(Marine Biological Lab, Woods Hole)

John D. Aber, Leader
Knut N. Nadelhoffer
Jerry M. Melillo

- Sulfur Mobility and Sulfur Budgets
(State Univ. of NY (SUNY) - Syracuse)
(University of Calgary, Canada)
(University of Illinois)
(State Univ. of NY (SUNY) - Plattsburg)

Myron J. Mitchell, Leader
H. R. Krouse
Mark B. David
Robert D. Fuller

- Organic Acids
(University of Illinois)

Mark B. David, Leader
Frank J. Stevenson
George F. Vance
Sandra Brown

TABLE 2. (CONTINUED)

o Modeling Support Group (Pacific Northwest Lab, Battelle N.W.)	Everett A. Jenne, Leader L. E. (Ted) Eary Don C. Girvin Lance W. Vail
o U.S. EPA/Environmental Research Lab-Corvallis (EPA)	Parker J. Wigington, Jr. Jeffrey J. Lee Daniel H. McKenzie Tim C. Strickland Heather E. Erickson
(NSI Technological Services Corp.) (Northrop Services, Inc.)	
o Scientific Oversight Committee (Oak Ridge National Laboratory) (Central Institute for Industrial Research, Norway) (Tetra Tech) (Lamont-Doherty Geological Observatory)	Dale W. Johnson Hans Martin Seip Steve Gherini Wallace Broecker
o Review Committee (Duke University) (U.S. Geological Survey) (Central Electricity Generating Board, UK) (Colorado State University) (University of Minnesota) (Electric Power Research Institute) (National Water Research Institute, Canada) (Oak Ridge National Laboratory) (Purdue University) (Temple University)	Dan Binkley Owen Bricker D. J. A. Brown James Gibson David Grigal John Huckabee David Lam Robert J. Luxmoore William McFee Woolcott Smith

Site Team --

The Maine Site Team has the following responsibilities in providing WMP data:

- Collection, preservation, preparation, and analysis of field solution samples (e.g., precipitation, throughfall);
- Distribution of appropriate field solution subsamples for aluminum, organic acid, and sulfur speciation;
- Collection, preparation, and distribution of soil samples to respective Task groups for analyses; and
- Implementation and documentation of appropriate QA/QC procedures associated with these activities.

Task Group --

Each of the six Task Groups has the following responsibilities in providing WMP analyses:

- Soil analyses for the characterization of soils at the watershed study site (discussed in Section 2);
- Specific analyses required to test and evaluate individual Task hypotheses (discussed in Section 2);
- Analyses of field solutions for aluminum, organic acid, and sulfur species by the respective Task Groups; and
- Implementation and documentation of appropriate QA/QC procedures associated with these activities.

EPA Management Team --

EPA personnel are responsible for project management and general administration of the WMP including:

- Defining Data Quality Objectives (DQOs) for model evaluation;
- Developing an integrated QA Plan;
- Providing QA/QC guidance and support including audit samples for both field solution and soil parameters;
- Ensuring integration of QA/QC procedures among Site and Task Groups;
- Training on field and laboratory QA/QC;
- Coordinating among Site and Task Groups; and
- Providing data management capabilities and support.

FIELD DESIGN

The WMP uses both large and small scale experimental manipulations to assess the effects of altered acidic deposition. Laboratory, plot, hillslope, and catchment scale experiments are being used to test and evaluate the WMP hypotheses and to gain a greater understanding of the process interactions that control surface water acidification and produce an integrated watershed response. Additional information on the design of field and laboratory experiments may be found in the Field Implementation Plan, FY87-89 (Erickson et al., 1990).

Catchment/Plot Design

The BBWM research site is located on the south slopes of Lead Mountain in Hancock County, southeastern Maine (Figure 2). Catchment manipulation experiments will be paired, with one catchment (e.g., East Bear Brook) serving as a control, and the second catchment (e.g., West Bear Brook) as the experimental catchment for additions of acidifying substances. The manipulation is scheduled to begin in the fall of 1989 and should be conducted for a 2 to 5 year period, followed by a monitoring/recovery phase. Reference plots have been established to intensively monitor catchment responses during the manipulation and recovery periods (Figure 3).

Eighteen 15 x 15 m plots have been established on a hillslope adjacent to the catchments (Figure 3) as part of an acid irrigation experiment designed to evaluate dose response relationships for H_2SO_4 and HNO_3 amendments. All plots have been instrumented with throughfall collectors, soil air samplers, soil water samplers (lysimeters), and leaf litter collectors. Acid-applications to the plots began during the 1987 field season.

Sources of Data

Data collected and analyzed from the catchment and plot studies can be divided into five categories: basin characteristics, dry deposition, field solutions, soil and vegetation data, and Task or process-specific data.

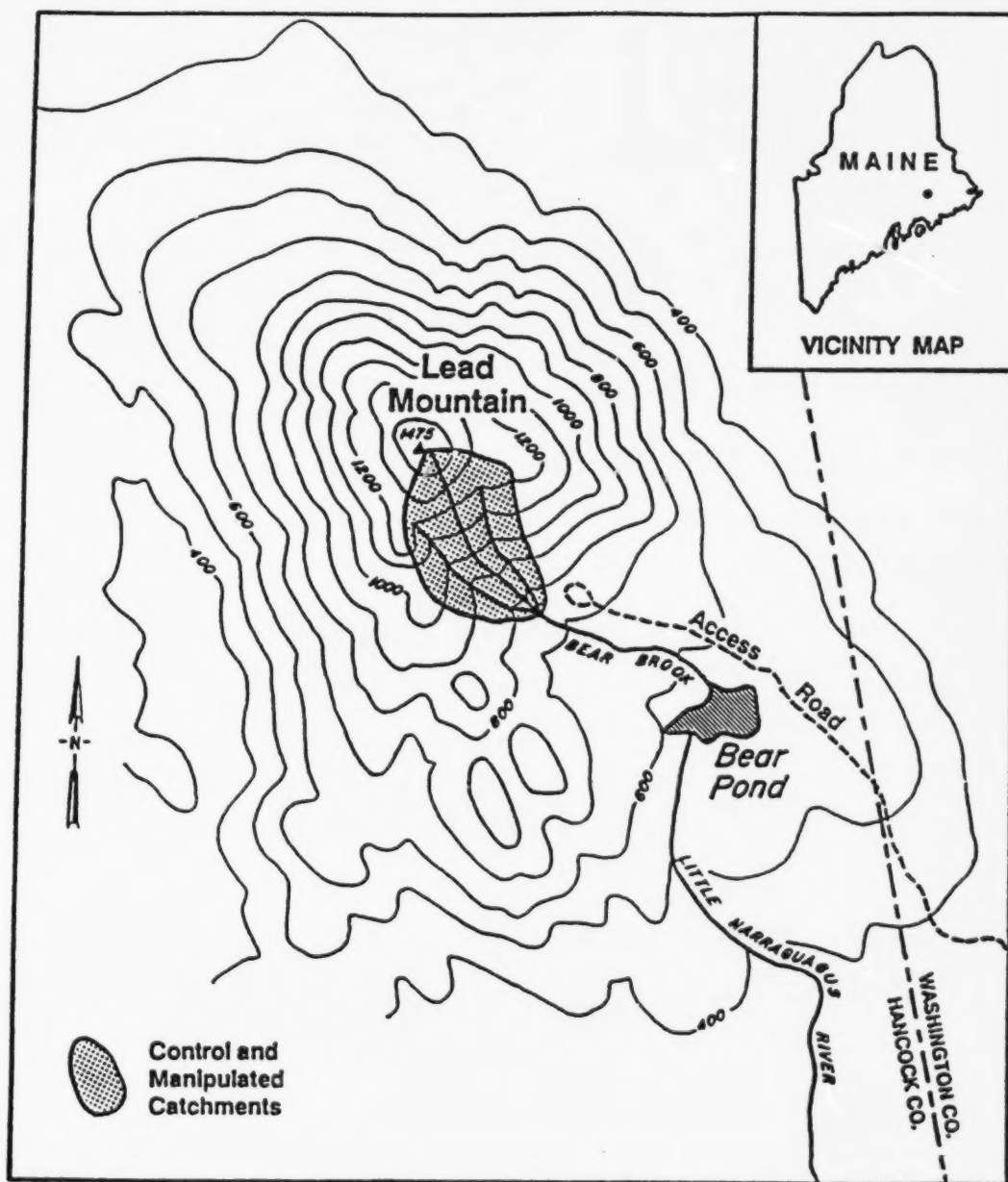


Figure 2. Location of Bear Brook Watersheds on Lead Mountain.



Figure 3. Location of Plots and Sampling Stations Within the Bear Brook Catchments.

Basin Characteristics --

Basin characteristics are defined by topographic information, depth to bedrock data, soil and vegetation surveys, geological maps, and other physical characteristics of the catchments. Soils in the study area were mapped during 1987 in a first order soil survey conducted jointly by U.S. Department of Agriculture (USDA) Soil Conservation Service (SCS) and the Maine Site Team. A topographic survey, a depth to bedrock survey and bedrock mapping effort were also carried out during that year. Resulting topographic, soil and depth to bedrock maps of BBWM were produced by ERL-C.

Dry Deposition --

A dry deposition monitor is planned for installation at the Bear Brook site. This monitoring station should collect meteorological data, and quantify sulfur, nitrogen and cation deposition. Plans are for the Maine Site Team to collect the dry deposition samples and forward these to the Atmospheric Sciences Research Laboratory - Research Triangle Park (ASRL-RTP) laboratory contractor, Environmental Science and Engineering, for analyses.

Field Solutions --

Field solution samples are defined as any sample in a soluble phase at the time of collection from the catchment. Field solution samples include precipitation, throughfall, stemflow, snowmelt, snow lysimeter solutions, soil water, stream water and groundwater. All field solution samples are collected by the Maine Site Team. Collection frequencies for each type of field solution and the resulting number of samples are given in Tables 3a and b. The Maine site laboratory performs all of the solution analyses except for aluminum fractions, fluoride, sulfur fractions and organic species, which are currently being analyzed by the Aluminum, Sulfur and Organic Acids Tasks. Total aluminum is measured by both the Maine Site and the Aluminum Task, although their methods of sample preparation differ. The Maine Site filters ($0.4 \mu\text{m}$) and acidifies (HNO_3) aluminum samples prior to analysis. The Aluminum Task measures aluminum on an unfiltered, unacidified sample. Table 4 lists the parameters that each group measures and the analytical methods used.

TABLE 3A. MAXIMUM MONTHLY SAMPLE COLLECTIONS FROM BEAR BROOK WATERSHED SNOW-FREE SEASON*

Sample Type	Week 1 (ext'l)	Week 2 (int'l)	Week 3 (ext'l)	Week 4 (int'l)	Seasonal Total
Streams	4	4	4	4	112
Bear Pond	1	0	0	0	7
ISCOs**	0	0	0	12	84
Internal Wells	3	3	3	3	84
External Plot wells	0	0	18	9	182
Precipitation	4	4	4	4	112
Throughfall	18	9	18	9	378
Stemflow	0	9	0	9	126
Tension Lys.	36	18	0	0	378
ZTL's ¹	0	0	36	18	378
IRS ² throughfall***	0	18	0	0	126
IRS carbon and tank samples ****	10	10	10	10	280
Weathering plots*****	12	0	0	0	84
Total	88	81	3	84	2422

* the snow-free season is assumed to last from May through November

** actual number dependent on events

*** ARAS pH, anions, and cations only

**** pH and anions only

***** no ANC or DOC

¹ Zero tension lysimeters

² Irrigation system on external plots

TABLE 3B. MAXIMUM MONTHLY SAMPLE COLLECTIONS FROM BEAR BROOK WATERSHED WINTER SEASON*

Sample Type	Week 1 (ext'l)	Week 2 (int'l)	Week 3 (ext'l)	Week 4 (int'l)	Seasonal Total
Streams	4	4	4	4	80
Bear Brook	1	0	0	0	5
ISCOs**	0	0	0	12	60
Internal Wells	3	3	3	3	60
External Plot wells	0	0	18	9	135
Precipitation	4	4	4	4	80
Throughfall	3	9	3	9	120
Stemflow	0	0	0	0	0
Tension Lys.	36	18	0	0	270
ZTL's ¹	0	0	36	18	270
IRS ² throughfall	0	0	0	0	0
IRS carbon and tank samples	0	0	0	0	0
Weathering plots	0	0	0	0	0
Snowmelt lysimeters**	8	8	8	8	160
Total	59	52	76	73	1300
Annual Total					3722

* the winter season is assumed to last from December through April

** actual number dependent on events

¹ Zero tension lysimeters

² Irrigation system on external plots

TABLE 4. FIELD SOLUTION SAMPLES: ANALYTICAL RESPONSIBILITY, PARAMETERS AND ANALYTICAL METHODS

MAINE SITE LABORATORY ANALYSES

<u>Parameters</u>	<u>Analytical Method Information</u>
Acid Neutralizing Capacity (ANC)	Gran Titration, Driscoll & Bisogni (1983)
Anions: SO ₄ , NO ₃ , Cl, F	IC ¹ , Tabatabai & Dick (1983)
Cations: Ca, Mg, Na, K	AAS ² , Hillman et al. (1986)
Dissolved Organic Carbon (DOC)	OI, EPA 415.2, direct injection
Dissolved Inorganic Carbon (DIC)	OI, Hillman et al. (1986), direct injection
Ammonium (NH ₄)	Autoanalyzer, Hillman et al. (1986)
Aluminum (Al)	AAS ³
Silica (Si)	Autoanalyzer, Hillman et al. (1986)
pH, closed	Electrode, Hillman et al. (1986)
pH, aerated	Electrode, Hillman et al. (1986)
Specific conductance	Wheatstone Bridge, Hillman et al. (1986)
True color	Optical comparator on filtered sample
Apparent color	Optical comparator on unfiltered sample

ALUMINUM TASK LABORATORY ANALYSES

<u>Parameters</u>	<u>Analytical Method Information</u>
Al-Monomeric	AAS, Driscoll (1984)
Al-Total	AAS, Hillman et al. (1986)
Fluoride	Ion selective electrode

(Continued)

TABLE 4. (Continued)

ORGANIC ACIDS TASK LABORATORY ANALYSES

<u>Parameters</u>	<u>Analytical Method Information</u>
Carbon - organic fractions	Leenheer (1985)
DOC	Dohrman (1984), EPA 415.2

SULFUR TASK LABORATORY ANALYSES

<u>Parameters</u>	<u>Analytical Method Information</u>
Sulfur - fractions	Landers et al. (1983)

¹ Ion Chromatograph

² Atomic Absorption Spectrophotometer; Ca and Mg with N_2O - acetylene flame, Na and K with air-acetylene flame.

³ Atomic Absorption Spectrophotometer; Al with furnace.

Soil-Vegetation Characterization Data –

Soil samples from both the catchment and plot experiments are analyzed for specific parameters by the Task Groups (Table 5). Soil samples were collected from the external plots, the series plots, and the benchmark pits during the initial phase of the WMP. To assess the response of soils to experimental manipulation, a buried soil bag experiment was designed by project scientists using a homogenized standard soil enclosed in nylon mesh bags, relocated in the field and retrieved for analysis throughout the project. Chemical analyses are being performed on foliage and litter samples as described in Table 6.

Task-Specific Data –

Each Task addresses a specific set of hypotheses. The analytical methods used by each Task have been selected either to maintain comparability with other methods used within the AERP or because of a method's unique attribute for testing a given hypothesis. Each method meets the necessary QA requirements specified in the Task plans (Appendix C). Sample types, parameters, analytical methods and Task laboratories are listed in Table 7.

TABLE 5. BEAR BROOK SOIL CHARACTERIZATION¹

Parameter	Task or Site Responsible	Analytical Method Information
Al-Exchange	Aluminum	Juo & Kamprath (1979), Bloom et al. (1979),
Al-Extract	Aluminum	Cappo et al. (1986)
C-Total organic	Organic acids	LECO Analyzer
CEC	Aluminum	NaCl, Rhoades (1982)
Exch. acidity	Aluminum	KCl, Robarge & Fernandez (1986)
Exch. bases	Aluminum	NH ₄ Cl, Thomas (1982)
Fe-Extract.	Aluminum	Cappo et al. (1986)
Fulvic Acid	Organic acids	Schnitzer (1982)
Humic Acid	Organic acids	Schnitzer (1982)
N-Total	Nitrogen	Modified Kjeldahl, Auto Analyzer
pH	Aluminum	DI, CaCl ₂ , USDA/SCS (1984)
S-Fractions	Sulfur	Landers et al. (1983)
S-Total	Sulfur	Landers et al. (1983)
Lime potential	Maine Site	CaCl ₂ extraction, Cappo et al. (1986)
Soil texture	Maine Site	Sieving & gravimetric, USDA/SCS (1984)
Soil structure	Maine Site	Visual, USDA/SCS (1984)
Bulk density	Maine Site	Clod method, USDA/SCS (1984)
Horizon thickness	Maine Site	Visual, USDA/SCS (1984)
Coarse fragment content	Maine Site	Sieving, Hamburg (1984)

¹ Soil characterization will be performed several times during the project.

TABLE 6. BEAR BROOK FOLIAR AND LITTER CHEMICAL ANALYSES

Parameter	Task or Site Responsible	Analytical Method Information
S-Total	Sulfur	Landers et al. (1983)
N-Total	Nitrogen	Kjeldahl/Auto Analyzer
Cations	Maine Site	AAS

TABLE 7. TASK ANALYSES

Task Area (Laboratory)	Parameter	Sample Type	Method Information
Cation Resupply (Drever)	Base Cations	Soil (weathering plots)	AAS*, ICP** NH ₄ Cl Extraction
	CEC	Soil (weathering plots)	AAS, NH ₄ Cl Extraction
	Exch. Acidity	Soil (weathering plots)	AAS, KCl Extraction
	pH	Soil (weathering plots)	Electrode
	Al-Total	Soil extract	ICP
	Anions	Soil extract	IC***
	Base cations	Soil extract	AAS
	pH	Soil column	Electrode
	Si	Soil extract	ICP
Cation Resupply (Schnoor)	Al-Total	Soil extract	AAS, EPA Method 202.2
	ANC	Soil extract	Gran titration
	Anions	Soil extract	IC
	Base cations	Soil extract	AAS, IC
	DOC	Soil extract	Dohrman Carbon Analyzer
	NH ₄	Soil extract	IC
	pH	Soil extract	Electrode
	Si	Soil extract	Colorimetry, APHA (1980)
Aluminum (Driscoll)	Al-Total	Soil column	AAS, EPA Method 202.2
	Anions	Soil column	IC, Small et al. (1975) (F:ISE)
	Base cations	Soil column	AAS, Slavin (1968)
	DOC	Soil column	Dohrman, EPA Method 415.2
	NH ₄	Soil column	IC, Small et al. (1975)
	pH	Soil column	Electrode
	Si	Soil column	Autoanalyzer

* AAS = Atomic absorption spectrophotometry

** ICP = Inductively coupled plasma emission spectrometer

*** IC = Ion chromatograph

(Continued)

TABLE 7. (Continued)

Task Area (Laboratory)	Parameter	Sample Type	Method Information*
Sulfur (Mitchell)	Al-Total	Soil extract	AAS*, EPA Method 202.2
	ANC	Soil extract	Gran Titration
	Anions	Soil extract	IC*** (No F)
	Base cations	Soil extract	AAS
	DOC	Soil extract	Dohrman, EPA Method 415.2
	Fe	Soil extract	AAS, EPA Method 236.1
	NH ₄	Soil extract	Autoanalyzer or Wescon Analyzer
	pH	Soil extract	Electrode
	S-Fractions	Soil extract	Landers et al.(1983)
	S-Total	Soil extract	Landers et al.(1983)
	Sp. cond.	Soil extract	Wheatstone Bridge
Organic Acids (David)	Al-Total	Soil column	AAS, EPA Method 202.2
	Al-Total ext.	Soil column	AAS, Barnes (1975)
	ANC	Soil column	Gran titration
	Anions	Soil column	IC, (F:ISE)
	Base cations	Soil column	AAS
	CO ₂	Gas	NaOH
	DOC	Soil column	Dohrman, EPA Method 415.2
	Fe	Soil column	AAS, EPA Method 236.1
	NH ₄	Soil column	Steam distillation, Kenney and Nelson (1982)
	pH	Soil column	Electrode
	Sp. cond.	Soil column	Wheatstone Bridge
Nitrogen (Aber)	NH ₄	Soil extract	Autoanalyzer, KCL extract
	NO ₃	Soil extract	Autoanalyzer, KCL extract

* AAS = Atomic absorption spectrophotometry

** ICP = Inductively coupled plasma emission spectrometer

*** IC = Ion chromatograph

SECTION 3

DATA QUALITY OBJECTIVES AND QUALITY ASSURANCE OBJECTIVES

DATA QUALITY OBJECTIVES FOR MODEL EVALUATION

The DQOs identify project objectives, evaluate the underlying hypotheses, experiments, and tests to be performed, and then establish guidelines for the quality of the data required to achieve these objectives. The approach to evaluation of the DDRP dynamic watershed models was discussed in the document entitled Watershed Manipulation Project: Rationale for Hypothesis Formulation and Testing (Thornton and Wigington, 1990). As discussed previously, a major reason for conducting the WMP is to provide data of known quality to evaluate the various DDRP models, assess their uncertainty, and estimate the possible misclassification of forecast watershed response. Thus the rationale document specifically addresses objectives for model evaluation.

QUALITY ASSURANCE OBJECTIVES

Data of known and documented quality are necessary to meet all WMP objectives. Quality assurance objectives for the WMP are defined in terms of the following characteristics:

- Precision
- Accuracy
- Comparability
- Representativeness
- Completeness

which are defined below.

Precision

Precision is a measure of mutual agreement among individual measurements of the same property. The Coefficient of Variation (CV), also known as the percent Relative Standard Deviation (RSD), is used to express precision.

Where: $CV = (s/\bar{x}) * 100$
 s = sample standard deviation
 $\bar{x}$ = arithmetic mean

Accuracy

Accuracy is the degree of agreement of a measurement (or an average of measurements) X , with an accepted reference or true value, T . It is alternatively termed bias. Accuracy is expressed as the percent difference from the true value ($100 (X-T/T)$), unless spiking materials are used and percent recovery is calculated (Section 4).

Comparability

Comparability is defined as the confidence with which one data set can be compared to another. Comparability of data from the WMP to similar data from other projects is emphasized, in addition to comparability of data sets generated within the WMP. Comparability of solution analyses is evaluated primarily through the use of performance evaluation samples sent to all cooperators on a quarterly frequency. Comparability of soil analyses is evaluated primarily through the use of internal quality control check samples of known concentrations. These programs are further discussed in Section 5.

Representativeness

Representativeness can be defined both qualitatively and quantitatively, and is dependent upon the experimental design and choice of sampling methods. The desired degree of representativeness is important in planning for the collection of samples and the subsequent uses of the data. A relevant sampling design issue, for example, is to determine how a sample will be collected to ensure it is representative of the desired characteristic (e.g., collecting grab samples in a restricted zone of a stream compared to complete transect sampling). Representativeness is a primary consideration of the WMP experimental and sampling design, and has been addressed more fully in the Field Implementation Plan (Erickson et al., 1990).

Completeness

Completeness is defined as the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under anticipated sampling/analytical conditions. After validation, the percentage of valid data required for broad groups of data types are:

- Hydrometeorological-90%;
- Water chemistry-90%;
- Soil and soil solution analyses-75%;
- Biological analysis-80% (Thornton and Wigington, 1990). If in-coming data represent less

than the specified percentage expected, sampling and handling procedures will be reviewed and appropriate steps will be taken to increase completeness.

Quality Assurance Objectives for Sample Types

Quality assurance objectives (precision and accuracy) are defined at the analytical level for each parameter and sample type in the WMP. The QA objectives may be amended after evaluation by the Maine Site Team, the EPA Management Team and the Scientific Oversight Committee (Table 2). QA objectives for the WMP are listed as follows:

- Dry deposition (Table 8)
- Field solutions (Table 9)
- Soil analyses (Table 10)
- Task analyses (Section 3) of each Task QA Plan (Appendix C).

The strategy for assessing the WMP QA objectives is to use an integrated approach, which is outlined in the remainder of this document.

TABLE 8. QUALITY ASSURANCE OBJECTIVES FOR DRY DEPOSITION

Parameter	Units	Expected Range	Accuracy	Precision	Completeness
Particulate NO₃/SO₄					
SSI ¹	µg/m ³	10-1000	10%	20%	70%
47 mm TF/PC ²	µg/m ³	10-1000	10%	20%	90%
NO₃					
47 mm TF/PC	µg/m ³	1 to 25	20%	20%	90%
SO₂					
47 mm TF/PC	µg/m ³	1 to 75	20%	20%	90%
Meteorological					
Wind speed	m/s	0 to 75	2%	2%	90%
Wind direction	deg	0 to 360	2%	2%	90%
Dew point	0 °C	-30 to 70	2%	5%	90%
Solar radiation	watts/m ²	-	-	-	-
Ambient temperature	°C	-20 to 50	1 °C	2 °C	90%

¹ PM₁₀ Size Selective Inlet High Volume Sampler

² Teflon/Polycarbonate Filter

TABLE 9. QUALITY ASSURANCE OBJECTIVES FOR FIELD SOLUTION SAMPLES

Parameter	Units	Expected Range	Reporting Format	Relative or Absolute Precision Goal ¹	Relative or Absolute Accuracy Goal ¹
True Color	pcu ³	0-250	0	5%, $\pm 5^2$	10%, $\pm 10^2$
pH, closed	S.U. ⁴	3-8	0.00	± 0.05	± 0.1
pH, aerated	S.U.	3-8	0.00	± 0.05	± 0.1
ANC	$\mu\text{eq/L}$	-100-500	0.0	5%, ± 5	7%, ± 5
Specific conductance	$\mu\text{S/cm}$	5-1000	0.0	5%, ± 1.0	10%, ± 2.0
DOC	$\mu\text{mol C/L}$	0.1-50	0.0	5%, ± 17	10%, ± 33
DIC	$\mu\text{mol C/L}$	0.1-20	0.0	5%, ± 17	5%, ± 33
Ca ²⁺	$\mu\text{eq/L}$	9.0-1000	0.	5%, ± 5.0	5%, ± 5.0
Mg ²⁺	$\mu\text{eq/L}$	8.0-600	0.	5%, ± 8.2	10%, ± 8.2
K ⁺	$\mu\text{eq/L}$	2.0-25	0.0	10%, ± 1.3	10%, ± 2.6
Na ⁺	$\mu\text{eq/L}$	20-300	0.	5%, ± 4.4	10%, ± 4.4
NH ₄ ⁺	$\mu\text{eq/L}$	0-100	0.0	5%	10%
SO ₄ ²⁻	$\mu\text{eq/L}$	20-400	0.	5%, ± 3	7%, ± 5
Cl ⁻	$\mu\text{eq/L}$	5-300	0.0	5%, ± 3	7%, ± 5
NO ₃ ⁻	$\mu\text{eq/L}$	0-80	0.0	5%, ± 1	7%, ± 2
F ⁻	$\mu\text{eq/L}$	0-10	0.0	5%, ± 3	10%, ± 3
Si	$\mu\text{mol/L}$	0.1-25	0.	5%, ± 7	10%, ± 14
Al:					
Total	$\mu\text{mole/L}$	1-40	0.0	10%, ± 0.2	15%, ± 0.4
Monomeric	$\mu\text{mole/L}$	1-40	0.0	10%, ± 0.2	15%, ± 0.4
Non-labile	$\mu\text{mole/L}$	1-40	0.0	10%, ± 0.2	15%, ± 0.4

¹ Unless otherwise noted, this is relative precision or accuracy at concentrations above (about 10 times) instrumental detection limits.

² Absolute precision or accuracy goal in terms of applicable units.

³ Platinum cobalt units.

⁴ Standard pH units.

TABLE 10. QA OBJECTIVES FOR SOIL ANALYSES

Parameter	Units	Reporting Format	Expected Range	Lower Range	Precision at Lower Range	Upper Range	Precision at Upper Range
pH in water	S.U. ¹	0.01	2.50-7.50	-	±0.15 ²	-	±0.15 ²
pH in 0.01 M CaCl ₂	S.U.	0.01	2.50-7.50	-	±0.15	-	±0.15
pH in .002 M CaCl ₂	S.U.	•	•	-	•	-	•
Total organic C	g/Kg	0.01	0-7.50	0-5.0	±0.5	>5.0	10%
Humic acid	•	0.01	•	•	±0.5	>2.5	20%
Fulvic acid	•	0.01	0-130	•	±0.5	•	20%
Total N	•	0.01	0-30	0-1.5	±0.15	1.5	10%
Total S	g/Kg	0.001	0-2.41	0-0.2	±0.02	.2	10%
Extractable S, H ₂ O or PO ₄	mg/Kg	0.01	1-120	1-15	1.5	15.0	10%
CEC (NH ₄ Cl)	cmol ⁺ /Kg	.001	0-50	0.2-2.5	±0.25	>2.5	10%
Exchangeable Ca (NH ₄ Cl)	•	•	0-50	0-0.2	±0.02	>0.2	10%
• Mg	•	•	0-10	0-0.2	•	>0.2	•
• Na	•	•	0-1	0-0.2	•	>0.2	•
• K	•	•	0-5	0-0.2	•	>0.2	•
Exchangeable acidity (BaCl ₂ -TEA)	cmol ⁺ /Kg	0.01	0-50	0-6.7	±1.0	>6.7	15%
Exchangeable Al (NH ₄ Cl)	cmol ⁺ /Kg	0.01	0-10	0-1.3	±0.2	>1.3	13%
Fe ³	% dry wt.	0.01	0-1.0	0-0.30	±0.03	7.3	10%
Al ³	% dry wt.	0.01	0-6	0-0.30	±0.03	>.3	10%
Bulk density	g/cm ³	0.1	0.2-2.0	-	± 0.1	-	±0.1

¹ Standard pH units.² Absolute precision goal in terms of applicable units.³ Extractable by pyrophosphate, acid-oxalate, or citrate-dithionite.

SECTION 4

INTEGRATED QUALITY ASSURANCE PROGRAM

QUALITY ASSURANCE INTEGRATION

The WMP is designed as an interactive, interdisciplinary project. An integrated QA/QC program is essential for the WMP because:

- Different laboratories are performing analyses;
- Data from each of these laboratories are required by other Site/Task Groups to address different hypotheses;
- Data from all laboratories are required to achieve the WMP objectives; and
- Data of known and documented quality are required throughout the Project.

Three approaches are used to integrate QA in the WMP:

- Standardized field sampling and preparation protocols;
- Establishment of interlaboratory comparisons; and
- Appropriate intralaboratory QA/QC.

Field sampling and sample preparation protocols follow DDRP and National Surface Water Survey (NSWS) methods whenever possible. Methods developed within the WMP are documented and maintained throughout the project. Measurements of precision and accuracy using a number of QC samples describe and assess inter- and intralaboratory variability, building on the basic approaches for assessing precision and accuracy illustrated in Figures 4 and 5.

Field Sampling and Preparation

QA procedures are initiated prior to field sampling and continue through data management and analysis. The purpose of sampling and preparation QA is to ensure that data collected in the field are representative, complete, and comparable with field data collected at different times. The primary group responsible for field sampling is the Maine Site Team. Protocols for field sampling and preparation protocol and QA are discussed in Section 6. Training, workshops, and site audits will be used to meet QA objectives in field sampling and to document field sampling and preparation protocol.

LEVELS OF PRECISION

<u>Phase of Data Collection</u>			<u>QA Data Interpretation</u>
Sample Collection	Sample Preparation	Sample Analysis	
Collocated Samples			Best estimates of intra- or interlaboratory precision of the entire measurement system.
Field Replicate			Second best estimate of intra-laboratory precision of measurement system from sample acquisition through analysis.
Field Split			Second best estimate of inter-laboratory precision of the measurement system from sample analysis.
	Lab Replicate		Best estimate of interlab- oratory precision of sample pre- paration and analysis.
	Lab Split		Best estimate of interlaboratory precision of sample preparation and analysis.
		Analysis Replicate	Estimate of intralaboratory precision of analysis.
		Analysis Split	Estimate of intralaboratory precision of analysis.

Figure 4. Sample phase and evaluation of precision. (Modified from QAMS, 1984).

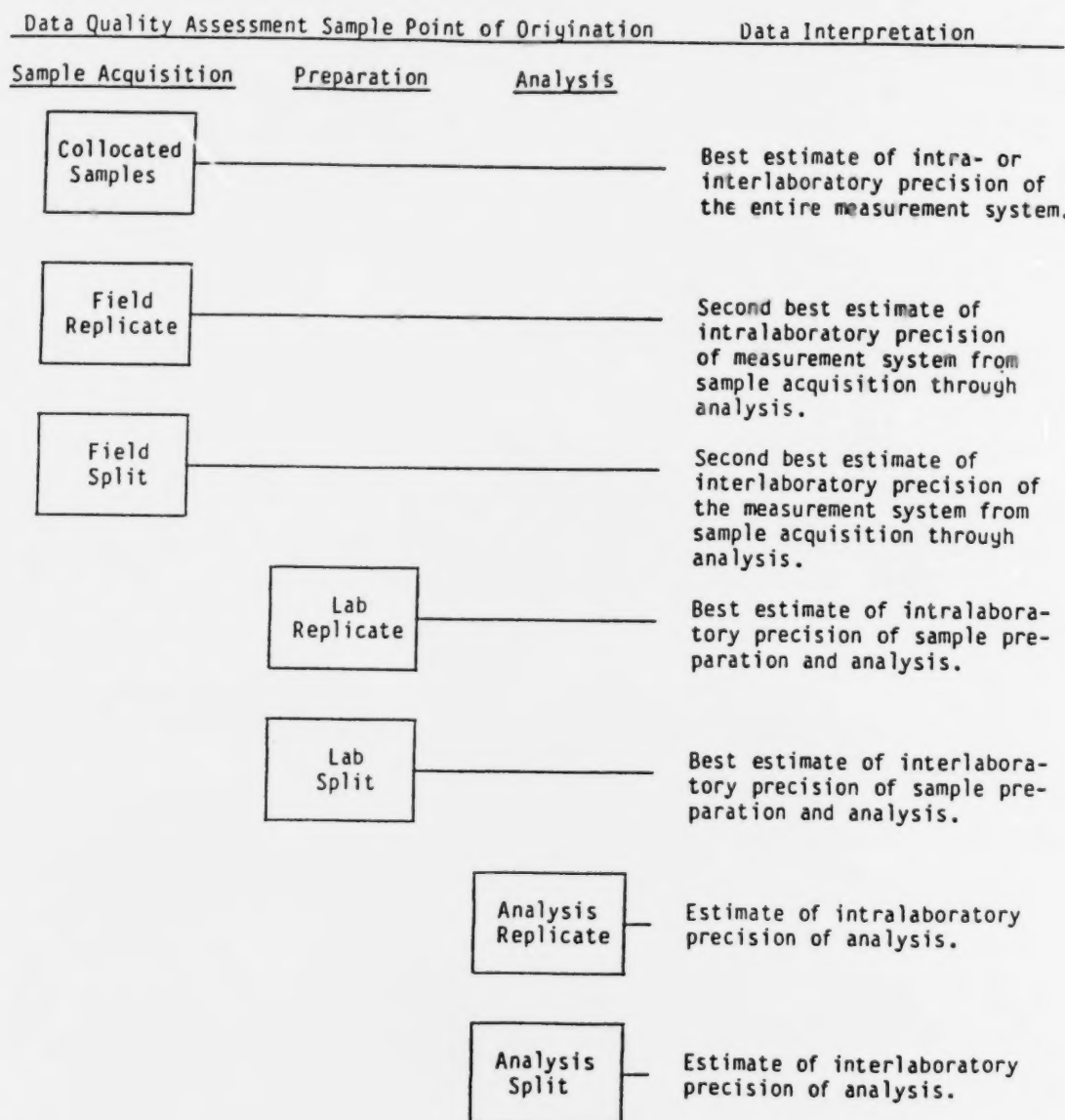


Figure 5. The use of target analyte spikes for bias estimation (QAMS, 1984).

Interlaboratory Comparisons

Interlaboratory comparisons ensure that data collected in different laboratories of the WMP are comparable. The type and frequency of interlaboratory comparisons varies depending on the kind of data collected (e.g., field solutions, soil, or Task-specific data) and the number of laboratories involved in the analyses. The Maine Site Team, for example, will analyze most of the field solution samples so interlaboratory comparisons for these samples are not critical. In this case, intralaboratory comparisons can provide the necessary QA information to maintain and assess data quality.

Intralaboratory Quality Assurance/Quality Control

Intralaboratory QA/QC ensures that data collected within the same laboratory are comparable over time and continue to satisfy the QA goals and DQOs. Intralaboratory comparisons are necessary to ensure that drifts in measurement systems have not occurred among sample batches during the course of the analyses, that detection limits are the same over all analyses and that variability in precision and accuracy is known and documented. Intralaboratory QC includes identifying sources of error and contamination, evaluating data at the time of analysis and ensuring that all analytical instrumentation is operating properly.

ASSESSMENT OF PRECISION AND ACCURACY

Inter- and intralaboratory QA concerns exist for each of the three data categories:

- Field solution data
- Soils/vegetation characterization data
- Task-specific data.

These concerns are addressed by ensuring that accuracy and precision objectives are being met at all times. Precision and accuracy (bias) will be assessed for the specific data categories at two different levels in the WMP:

- Analytical level (beginning just prior to analysis, includes analysis, data recording, data management and review)

- Measurement System level (including sampling, storage, transport, preparation, analysis, recording, etc.)

In a controlled system, analytical errors would be expected to be less than entire-measurement system errors. How these errors are assessed is the subject of the remainder of Section 4.

Field Solutions

Interlaboratory Comparisons –

The goal of interlaboratory comparisons for the field solutions data category is to assess differences in precision and accuracy among laboratories.

- Accuracy: Analytical Level - The Maine Site Team is responsible for analyzing all field solution samples except for aluminum fractions, and fluoride (Aluminum Task Laboratory), organic acids (Organic Acids Task Laboratory) and sulfur fractions (Sulfur Task). Dissolved organic carbon (DOC) and sulfate are normally analyzed by Maine for all field solution samples. The Organic Acids Task laboratory also measures DOC and the Sulfur Task laboratory also analyzes sulfate, but on a reduced frequency to coincide with their organic acid and sulfur fraction analyses. Total aluminum is measured by both the Maine Site and the Aluminum Task. Interlaboratory bias is assessed among all laboratories analyzing similar parameters. The bias estimates are made using synthetic audit samples provided on a quarterly basis to the participating laboratories.
- Precision: Analytical Level - Field solution aliquots are prepared by the Maine Site laboratory and shipped to the Aluminum, Organic Acids, and Sulfur Task laboratories. Aliquots from Maine are bulked or unbulked (depending on sample type) for these Task laboratories. Solution samples, arriving at the Maine laboratory, are split before analysis on a quarterly basis to assess interlaboratory precision for sulfate data between the Maine laboratory and the Sulfur Task laboratory; for DOC data between the Maine Site laboratory, the Organic Acids Task laboratory, and the Aluminum Task laboratory; and for aluminum data between the Maine Site laboratory and the Aluminum Task. When this occurs, the

samples are analyzed by the respective laboratories immediately (not composited) so as to allow for precision estimation.

Intralaboratory Comparisons –

Within-laboratory precision and bias assessment for the field solutions focuses primarily on the Maine laboratory because of its major role in the total sampling/analytical effort. Sulfur, Aluminum and Organic Acids Task analytical laboratories should follow the same quality assurance protocols established for field solutions. Potential contamination of field solutions by the sampling team is assessed with field blanks. Field blanks are deionized water (ASTM Class I) samples labelled and processed as normal samples from the field through the analytical process. Intralaboratory precision and accuracy for the field solutions will be continually monitored by the Maine Site group, and results reported to EPA (Section 7).

- Accuracy: Analytical Level - Accuracy estimates at the analytical level for field solutions (intralaboratory) are measured using blind performance audit samples issued to the Maine Site laboratory on a quarterly basis. The audit samples are in addition to the standard measurements of accuracy that are instituted on a per analytical run basis for each field solution parameter as discussed in Section 6. Performance audit samples also are issued to the Sulfur and Organic Acid Task laboratories on a quarterly basis, for sulfate and DOC bias assessment, respectively. Performance audit samples (sources, concentrations, etc.) are discussed further in Section 5.

Analytical bias at the intralaboratory level is also assessed by using laboratory spikes and calculating percent recoveries. Laboratory matrix spikes are prepared once per sampling period. A matrix spike is prepared by spiking an aliquot of a sample with a known quantity of analyte. The spike concentration is approximately equal to the endogenous level of the analyte, so that the resulting analyte concentration is approximately twice the endogenous

level of the analyte and within the linear range of calibration. Also, the volume of the spike added is negligible (less than or equal to 1/1000 of the sample aliquot volume).

Percent recovery of the spike is calculated as follows:

$$\% \text{ Spike Recovery} = \frac{\text{Value of sample plus spike} - \text{Value of unspiked sample}}{\text{Value of spike added}} \times 100$$

The spike recovery is 100 ± 15 percent. If the recovery is not within this range, two additional, different samples will be spiked, analyzed, and recoveries calculated.

- Precision: Analytical Level - Analytical level precision for the WMP laboratories analyzing field solution samples is estimated by using laboratory replicates, including replicates of performance audit samples. Analytical replicates are prepared and analyzed at a frequency equal to approximately 5 percent of the total sample number.
- Precision: Measurement System Level - Precision estimates for the entire Measurement System level are assessed by using collocated samples and duplicates or field replicates. Collocated samples are independently collected samples that include a component of inherent in-situ variability. Field replicates provide precision information about succeeding steps in the measurement process after sample acquisition, which includes effects of transport, storage, shipment, analysis and data processing. Details of assessment on precision estimates for the entire measurement system, or portions thereof, are included in Section 6.

Soil Characterization

Interlaboratory Comparisons for Soil Analyses –

The Site Team and several Task laboratories are participating in the Bear Brook soils characterization effort (Table 5). Samples are collected by the members from the Site Team, EPA, or a Task group, depending on which type of soil sample is collected. Soil sampling for the external plots

was conducted during the summer of 1987 by project cooperators. The soils were sampled by increments rather than by genetic horizons and are described by the following: the first increment sampled was the organic horizon(s), excluding leaf litter this included the Oa and/or Oe horizons; the second increment sampled, if thick enough, was the albic (E) horizon; the third increment sampled was the upper 2 cm of the B horizon; the fourth increment was the next 5 cm.; the fifth increment was the next 18 cm; the sixth increment was from the bottom of the fifth increment down to 5 cm above the pit floor; the seventh increment was sampled from the bottom of the pit up 5 cm. The bottom of the sampling pit was at 1 m or the top of bedrock or dense till.

Soil sampling and preparation for the benchmark pits is described in Appendix A (*Preparation and Quality Assurance of Soil Samples for Benchmark Pit Characterization for the WMP*). Modification of the sampling protocol may occur after consultation with WMP QA staff; comparability between WMP and DDRP will be stressed.

- Accuracy/Precision: Analytical Level - Responsibility for analyses has been divided between the different laboratories with parameters generally being unique to each laboratory. Because of this, interlaboratory bias and comparisons within the WMP are unnecessary. As exceptions may arise, the pertinent Task or Site groups need to inform the EPA of the activity and sample splits arranged for the requisite laboratories.
- An International Interlaboratory Comparison Study was conducted by Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV) to assess method and laboratory bias in soil characterization analyses (see Section 5). Four WMP laboratories participated in this study.

Intralaboratory Comparisons for Soil Analyses --

Field QA protocols for the WMP follow DDRP Soil Survey protocols, where applicable, to estimate precision. Through cooperation with the DDRP Quality Assurance Staff at EMSL-LV, a bulk soil sample was collected from BBWM and prepared as a standard soil. The soil, termed the Maine B reference soil (also called WMP B soil), was used as one of the soils in the International Interlaboratory Comparison

Study conducted by EMSL-LV, and therefore has been sufficiently well-characterized by a number of laboratories across the U.S. and Canada.

- **Accuracy: Analytical and Measurement Level** - Accuracy at the analytical level is assessed by the use of the Maine B reference soil as an internal check sample. Results are compared to reference values made available to WMP laboratories.

For WMP laboratories analyzing benchmark soils, accuracy at the preparation level is assessed by the use of additional audit material inserted into the sample batches prepared at the University of Maine. Audit materials and reference values were obtained from the DDRP QA program. Reference materials were not available for the 1987 collection of external plot soils, so accuracy could not be assessed for these samples.

- **Precision: Measurement System Level** - Precision estimates for the entire Measurement Level are assessed by the use of field duplicate samples (Figure 4). For all collection times and for all soil sample types (benchmark soil samples, external plot soils) approximately 5 percent of the samples are collected in duplicate. For these samples twice the normal volume is collected for chosen sampling points (determined a priori). Precision estimates are also made for the portion of the Measurement Level beginning with sample preparation, shipment, analysis, and data handling. After sample sieving and homogenization, a preparation duplicate is made by splitting the prepared sample in half, then treating each sub-sample similarly. Preparation duplicates are made for approximately 5 percent of the soil samples. When external plots were sampled in 1987, one preparation duplicate was prepared for each of the seven increments by personnel at the University of Maine.
- **Precision: Analytical Level** - To assess analytical precision, laboratory replicates are prepared from standard samples and from the Maine B reference soil used as an internal quality control check sample. Control charts should be used to document and track precision over time.

Specific QA/QC guidance has been provided to WMP laboratories involved in the benchmark characterization effort. This guidance is included in Appendix A.

Task Specific Analyses

Interlaboratory Comparisons –

Comparability of data collected by each Task is of primary importance in the WMP. Various Task hypotheses require multiple Task data in order to accept or reject null hypotheses. The goal of interlaboratory comparisons is to ensure comparability of data among the Tasks. Many Task measurements are unique and made as part of specific experiments to test process level hypotheses. Several Tasks, however, have parameters in common (Table 7). Interlaboratory precision and bias for these parameters is assessed through participation in the quarterly performance audit sample program. Blind synthetic performance audit samples for appropriate parameters are analyzed by each laboratory to assess analytical precision and bias. The EPA team evaluates the data from each participating laboratory to assess laboratory performance. Quarterly and annual synthesis reports are prepared by EPA and submitted to cooperating laboratories.

Intralaboratory Comparisons –

Intralaboratory analytical precision and accuracy are measured at regular intervals according to the individual Task plans (Appendix C) to ensure that QA objectives are being maintained. The WMP performance audit program and internal QC checks in each Task provide the means to assess precision and accuracy at the analytical level. Individual Task QA plans include descriptions of internal QC checks and frequencies for each laboratory. Summaries of internal QC checks for Task laboratories are listed in Tables 11A through 11E.

INTERNAL CHECKS AND CORRECTIVE ACTION

In order to detect possible problems with analytical instruments, reagents, calibration standards, and techniques, it is critical to carry a series of analytical QC checks through all chemical analyses. The

TABLE 11A. INTERNAL QUALITY CONTROL CHECKS FOR ALUMINUM TASK DATA

Parameter	Sample Flow Point	QC Sample Type	Frequency	QC Check
Cations, anions, NH ₄ , Si, DOC	Collection	Triplicate samples	5% of sample load	Precision
	Analysis	Calibration QC sample	1/analytical batch	Accuracy
	Data	Conductivity balance checks	all, when cations & anions are measured and organic concentrations are low	Errors
pH	Analysis	QC check - pH 4.7 standardized acid	1/analytical batch	Accuracy

TABLE 11B. INTERNAL QUALITY CONTROL CHECKS FOR CATION RESUPPLY TASK DATA

Parameter	Sample Flow Point	QC Sample Type	Frequency	QC Check
Cations, anions, NH ₄ , Si, DOC	Analysis	Calibration QC sample (high and low)	1 set/analytical batch	Accuracy
		Duplicate analysis	10% of sample load	Precision
	Preparation	Reagent blank	2/prep batch	
pH	Analysis	pH 4.7 standardized acid	2/analytical batch	Accuracy
ANC	Analysis	Standard solutions	1/analytical batch	Accuracy

TABLE 11C. INTERNAL QUALITY CONTROL CHECKS FOR NITROGEN TASK DATA

Parameter	Sample Flow Point	QC Sample Type	Frequency	QC Check
NH ₄ , NO ₃	Sampling and preparation	Cross-calibration of analytical batches by retaining and freezing standards	Everytime a new standard solution is prepared and everytime a color reagent is prepared	Precision
	Analysis	Laboratory replicate samples	4 during pilot study	Precision
	Analysis	Laboratory spiked samples	4/soil type or elevation level	Accuracy

TABLE 11D. INTERNAL QUALITY CONTROL CHECKS FOR ORGANIC ACID TASK DATA

Parameter	Sample Flow Point	QC Sample Type	Frequency	QC Check
Al-total, Al-total extr. cations, Fe, Anions (AAS,IC)	Analysis	Calibration QC sample	10% ¹	Accuracy
		Detection limit QC sample	2.5% ¹	
		Calibration blank	2.5% ¹	• •
NH ₄ , DOC, Al-total extr.	Preparation	Matrix spike	5% ¹	Accuracy
		Reagent blank	1/batch	Contamination
All	Collection	Duplicate samples collected	5% ¹	Precision
pH	Analysis	QC sample; pH 4.7 standardized acid	1/15 samples	Accuracy
Sp. Cond.	Analysis	QC sample; standard KCl solution	1/batch (daily)	Accuracy
ANC	Analysis	Standard acid solutions	Twice daily	Accuracy

¹ of sample load

TABLE 11E. INTERNAL QUALITY CONTROL CHECKS FOR SULFUR TASK DATA

Parameter	Sample Flow Point	QC Sample Type	Frequency	QC Check
Base cations, Al-total, Fe, NH ₄ Fe, NH ₄	Analysis	Calibration QC Sample	10% ¹	Accuracy Instrument Performance
		Detection limit QC	2.5% ¹	
		Calibration blank	2.5% ¹	Accuracy
		Matrix spike	5% ¹	
S-Fractions S-Total	Preparation	Reagent blank	1/batch	
All	Collection	Duplicate samples collected	5% ¹	Precision
pH	Analysis	QC sample; pH 4.7 standardized acid	daily	Accuracy
Sp. Cond.	Analysis	QC sample, standard KCl solution	daily	Accuracy

¹ of sample load

purpose of QC checks is to correct problems immediately on-site, as opposed to QA checks, which are primarily used to evaluate the level of assurance (overall quality) of the data, once analyses are completed.

QC checks include documenting holding times for each parameter and ensuring that holding times have not been exceeded. Table 12 lists detection limits, sample preservation and storage conditions, and holding times for each parameter measured on field solutions. The holding times presented here are the same as National Surface Water Survey protocol, except in several cases where the WMP requirement is more stringent. The WMP policy regarding holding times is that sample data collected for samples analyzed outside of recommended holding times are considered questionable and are flagged with a data qualifier (H) in the database. QA/QC protocols must allow for problems to be identified in time for reanalysis within the specified holding times.

QC checks also include collection and analysis of field blanks to detect contamination during sample preparation. Contamination is indicated when the concentration of a blank sample is more than twice the detection limit of that parameter (Table 12). Internal QA in the WMP includes procedures which check the correctness of the analyses. These procedures include checking cation-anion balances and specific conductance balances as described by Hillman et al. 1986.

Task and Site laboratories also maintain raw data associated with the WMP such as calibration calculations, strip charts, computer printouts, copies of analyst's log books, etc. These raw data are thoroughly reviewed by the Principal Investigators (PIs) or their appointed surrogates to ensure that:

- The laboratory maintains sufficient raw data to validate all sample results
- The raw data support all the analytical results
- The laboratory can support the required limit of detection
- The calibration range brackets sample concentrations
- Calibration curves are determined correctly
- Theoretical concentrations of QC checks and matrix spike solutions are appropriate with respect to the calibration range and observed sample concentration
- Laboratory notebooks are adequately maintained.

TABLE 12. FIELD SOLUTIONS: DETECTION LIMITS, SAMPLE PRESERVATION AND HOLDING TIMES

Parameter	Detection Limit	Sample Preservation	Recommended Holding Times	Maximum* Holding Time
Al:				
total	0.2 Bmol/l	Filter, acidify with HNO_3 to pH <2; store at room temp.	28 days	6 months
monomeric	*	• • •	Extraction within 24 hrs; analysis within 28 days	6 months
non-labile	*	• • •	• • •	6 months
Apparent color	na**	Store at 4AC	3 days	14 days
True color	na	Filter thru GF/F; store at 4AC	3 days	14 days
pH, closed	na	Store in syringe at 4AC	48 hours	7 days
pH, aerated	na	Store at 4AC	7 days	7 days
ANC	na	Store at 4AC	14 days	14 days
Specific conductance	†***	Store at 4AC	14 days	14 days
DOC	8.3 Bmol C/ml	Filter thru baked GF/F; acidify with H_2SO_4 to pH <2; store at 4AC	14 hours	14 days
DIC	8.3 Bmol C/ml	Sealed glass at 4AC	7 days	7 days
Ca^{2+}	0.5 Beq/l	Filter thru 0.4 Bm; acidify with HNO_3 to pH <2; store room temp.	28 days	6 months
Mg^{2+}	0.8 Beq/l			
K^+	0.2 Beq/l			
Na^+	0.4 Beq/l			
NH_4^+	0.5 Beq/l	Filter thru 0.4 Bm; acidify with H_2SO_4	7 days	14 days

(Continued)

- * = analysis made after maximum holding time will be flagged in the database
- ** na = not applicable
- *** = blank must be less than 1 BS/cm

TABLE 12. (continued)

Parameter	Detection Limit	Sample Preservation	Recommended Holding Times	Maximum* Holding Time
SO ₄ ²⁻	1 µeq/l	Filter thru 0.4 µm; store at 4° C	28 days	28 days
Cl ⁻	0.5 µeq/l	" " "	28 days	28 days
NO ₃ ⁻	0.2 µeq/l	" " "	7 days	7 days
F ⁻	0.5 µeq/l	" " "	28 days	28 days
Si	20 µmol/L	Filter thru 0.4 µm; acidify with HNO ₃ to pH <2; store room temp.	28 days	6 months
Organic carbon fractions	na	Store at 4° C	14 days	14 days
Sulfur fractions	na	Store at 4° C	28 days	28 days

- * = analysis made after maximum holding time will be flagged in the database
 ** na = not applicable
 *** = blank must be less than 1 µS/cm

The Site/Task Leaders or appointed surrogates confirm on a per-batch basis that each analysis is within specified control limits before the analytical data are reported. If QC results are out of control limits, the laboratory is required to take immediate corrective action (Section 6) and, when appropriate, re-analyze the samples in question.

DATA VERIFICATION, VALIDATION AND REPORTING

The ERL-C is responsible for providing the final data set(s) for the WMP. These data, which will eventually become public domain, are used in the interim by the WMP cooperators to address project goals. Prior to any release, these data undergo routine review and analysis to determine their quality. Several levels of QA identify potential errors.

Data quality assessment follows many of the guidelines used in National Stream Survey and is based upon data procured in accordance with the WMP Field Implementation Plan, FY87-89 (Erickson et al., 1990) and analyzed in accordance with the procedures referenced in Section 2. These plans insure that the five aspects of data quality (completeness, comparability, representativeness, accuracy and precision) are applicable to the data throughout all stages of the project.

The data pass through three distinct phases before they are released. These steps are outlined in Figure 6. The data are further refined at each step by applicable checks to monitor their quality. These phases and their associated checks are described further in the following subsections.

Raw Data (Phase 1)

The raw data consist of the collective data from all components of sampling and analysis. Range and reasonableness checks, data entry checks and other bench-level procedures to screen the data for problems are used during this phase. Raw data include chemistry results from streams, soils or air, meteorological data, field data and other types of data required by the project.

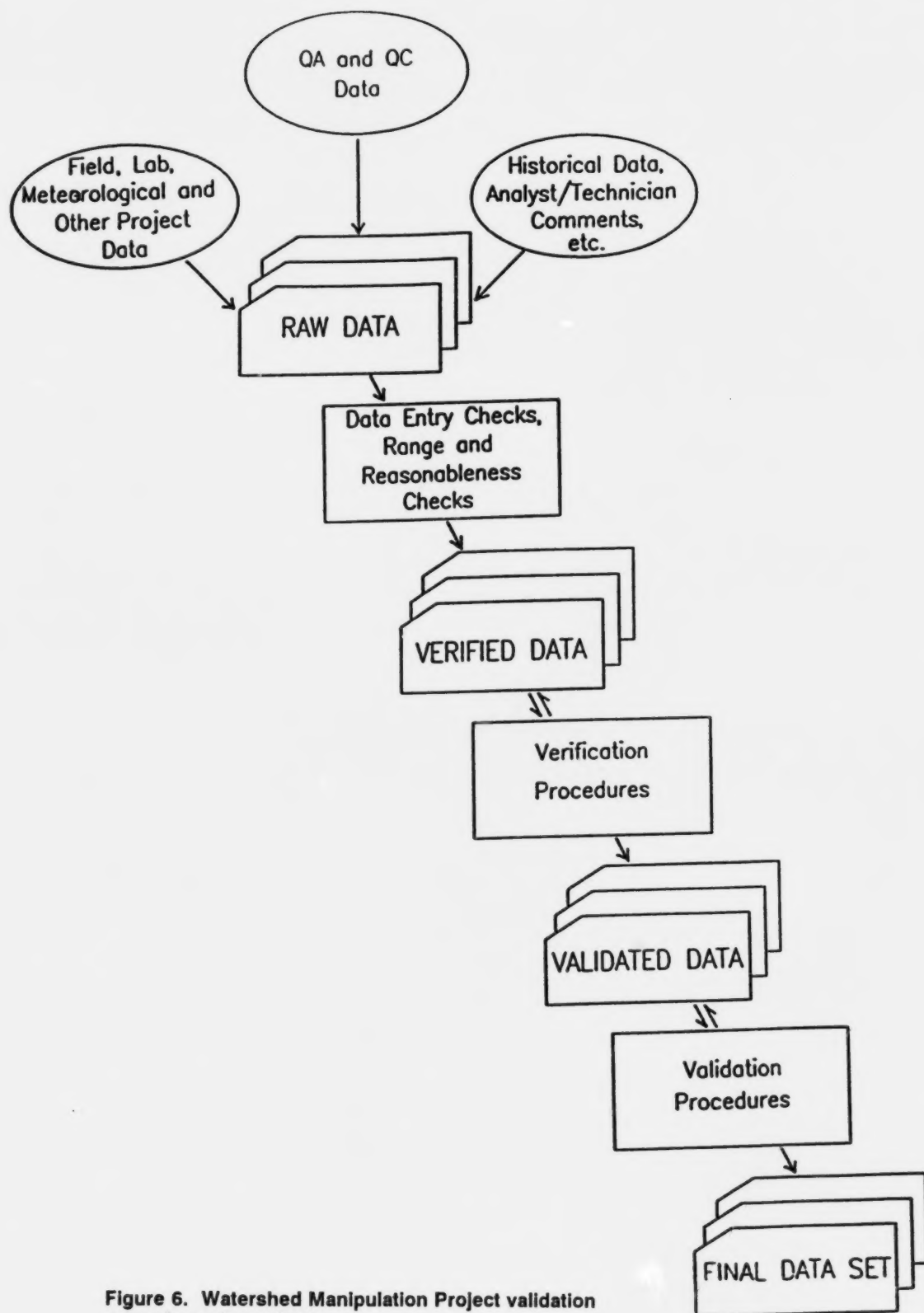


Figure 6. Watershed Manipulation Project validation procedures (overview).

Verified Data (Phase 2)

The screened, raw data are entered into a computer at the University of Maine, and a series of tests are performed on the data to identify, correct and flag raw data of questionable or unacceptable quality, and identify data that might need to be corrected during or after data validation. The verification procedures are designed to identify questionable data quickly enough to allow reanalysis before holding times are violated.

Tests used during the verification process include the calculation of ion balance, specific conductance and pH. For the complete list of verification procedures and the acceptable limits, see Table 13. Values outside of the acceptable limits defined in Table 13 indicate potential error and may be reanalyzed as a part of the verification process.

Verification, which is automated as much as possible with computer programs, occurs in two parts. The first is the identification of problems, errors and/or numeric changes. The second part actually makes and documents any changes and appends the data set with the appropriate flags or comments. The verification process, including these two parts, is illustrated by Figure 7. The verification procedures result in a data set that is qualified by the use of data quality flags. The verified data that are forwarded to ERL-C for validation contain all of the original raw data, results from any reanalysis, data quality flags, comments and other additions that result from the verification process. Specific information on data tracking and verification by the Maine Site group is included in Section 6.

Validated Data (Phase 3)

Data validation consists of reviewing the verification results and procedures, performing more advanced statistical analysis of the data and appending the resulting comments and flags to the final data set. It is important to understand that the validation procedures are performed in cooperation with the Maine site group and the final data set is the result of this cooperative effort. This process is summarized in Figure 8.

TABLE 13. TYPES OF ANALYSES PERFORMED DURING WMP DATA VERIFICATION

Ion Percent Difference:	Calculated according to Hillman et al., 1986. Assumes that the ratio of cations to anions is balanced. $IPD = \frac{(\text{sum of anions} - \text{sum of cations}) * 100}{(\text{sum of anions} + \text{sum of cations})}$ If total ionic strength is less than 100 $\mu\text{eq/l}$, samples are reanalyzed if IPD $\pm 30\%$. Otherwise, samples are reanalyzed if IPD exceeds $\pm 15\%$.
Calculated Conductance:	Calculated according to Hillman et al., 1986. Assumes that conductance can be approximated from ionic concentration.
Conductance Difference:	Calculated according to Hillman et al., 1986. Assumes that calculated conductance approximates measured conductance. $CPD = \frac{(\text{calc. cond.} - \text{meas. cond.}) * 100}{(\text{measured conductance})}$ If conductance is less than $\mu\text{mhos/cm}$ samples are reanalyzed if CPD exceeds $\pm 30\%$. Otherwise, samples are reanalyzed if CPD exceeds $\pm 20\%$.
Calculated pH:	Calculations developed by Maine site group. Assumes that pH can be approximated using ANC and DIC, after Hillman et al., 1986. Reanalysis may be necessary if calculated pH is less than equilibrated or closed-cell pH, or exceeds equilibrated pH by more than 0.5 pH units.
Spatial Analysis:	Samples may be reanalyzed if values are in disagreement with values from other comparable sites collected on the same day.
Temporal Analysis:	Samples are reanalyzed if time-series analysis indicates an anomalous value for the same stream site or lysimeter.
DQO Violations:	When sample volume permits, samples are subject to reanalysis if duplicated samples, laboratory splits, QC samples or other indicators of data quality exceed the limits defined in the WMP QA Plan.
Other Tests:	Other methods of screening the data during the verification process may be used at the University of Maine. These screening methods and appropriate formulas are supplied to ERL-C for review during data validation. Screening methods are based on known chemical relationships, site analysis and procedures.

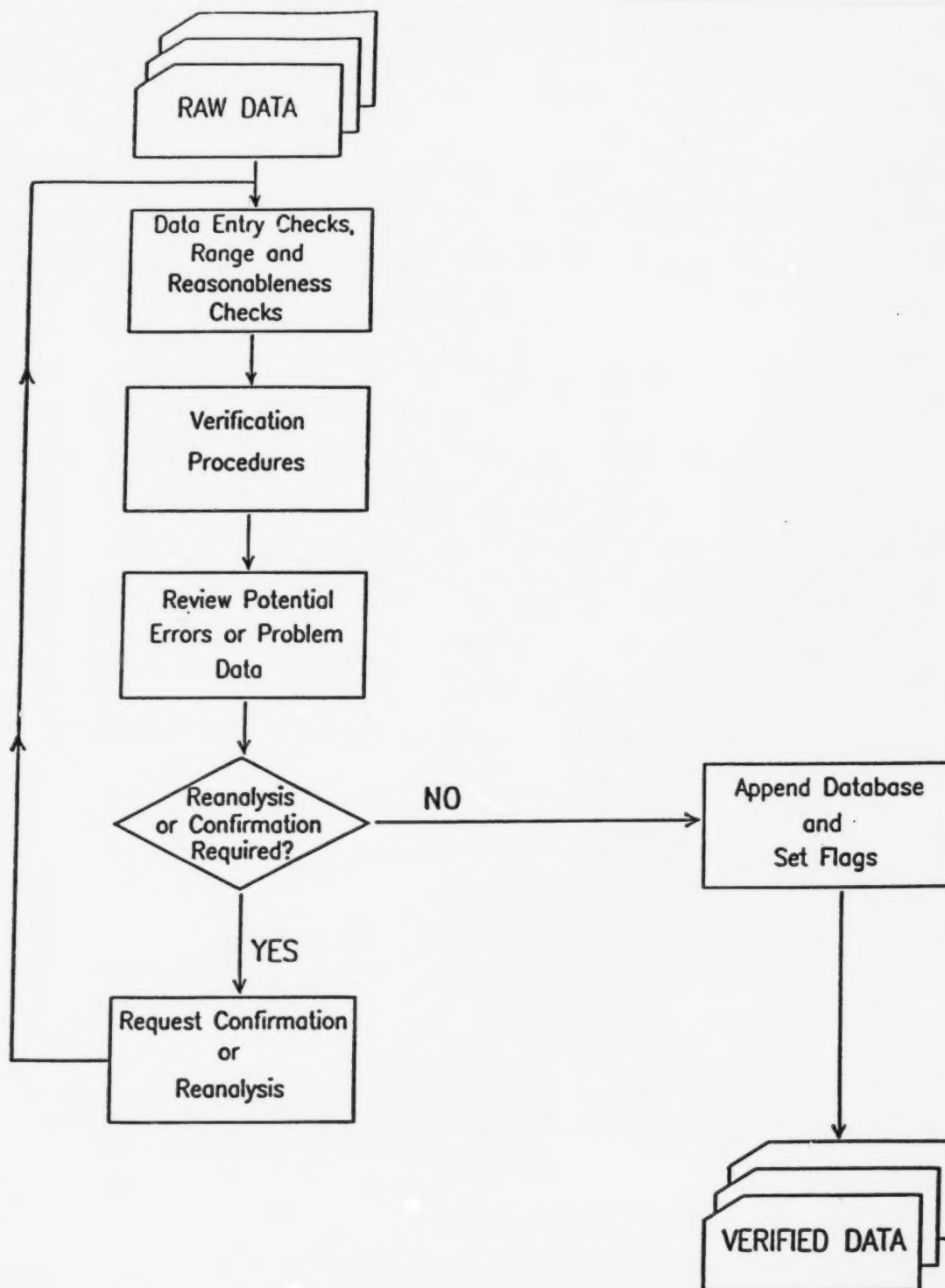


Figure 7. Watershed Manipulation Project verification procedures.

Although it is difficult, if not impossible, to maintain a single set of criteria which will identify all outliers or questionable data, general guidelines have been established for use by ERL-C in data validation. These guidelines are the same for all data sets and insure that the processes can be documented and repeated, if necessary. These steps are briefly discussed in the following paragraphs.

Prior to any statistical analysis or data manipulation is a thorough review of all information regarding data quality for the period of interest. All QA/QC, monthly and/or quarterly reports are scanned for problems or other factors influencing data quality. These factors include personnel changes, methods and instrument changes and operational conditions.

The data are then divided by type (stream, precipitation, lysimeter, etc.) and modified to facilitate statistical and graphical analysis. All replicates, duplicates and flags are removed. The data are converted to standard units and merged with meteorological and flow data, when appropriate. Calculated variables used for verification may be appended to these data sets.

With the aid of a computerized statistical software package (SAS or Systat), the data are analyzed using five procedures: summary statistics, box and whisker plots, correlation coefficients, residual analysis and graphical analysis. These tests are outlined in more detail in Table 14.

Each data point identified as a result of these steps is carefully reviewed. An attempt is made to determine if the value is the result of analytical, collection or transcription error, or can be attributed to a known event or occurrence. Of these, only analytical error (i.e., analytical equipment malfunctions) or collection error is likely to result in a final validation flag. Transcription or data entry errors are corrected prior to release of the final data set. Outliers which can not be attributed to any of the above are flagged in the final data. A data point will usually have to be identified in two or more validation tests to warrant rejection. A data point identified by only one test may be rejected, accepted or marked as questionable, depending on the degree of uncertainty around the value.

The validation flags are then determined (see next section), the rejected data are removed and the data are reanalyzed through the validation procedures. This reiteration is often useful in identifying outliers that were not apparent during the first pass. A review of the results and procedures may also identify additional groups, tests and/or comparisons which can be used in validation.

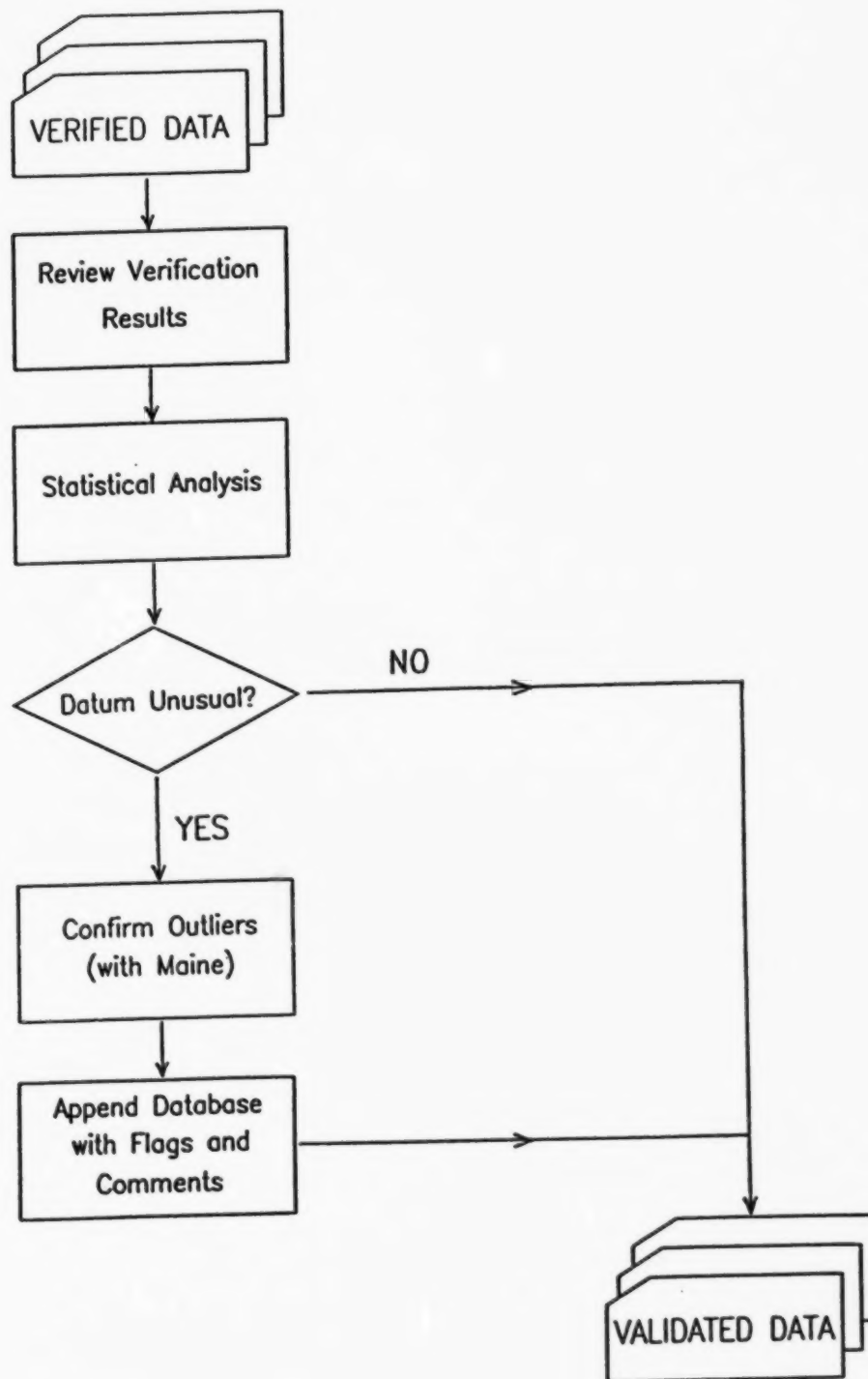


Figure 8. Watershed Manipulation Project validation procedures.

TABLE 14. TYPES OF ANALYSES PERFORMED DURING WMP DATA VALIDATION

Summary Statistics:	Mean, minimum, maximum, standard deviation and number of observations. These statistics are compared to those of previous data or other data sets to check for consistency, range and reasonableness.
Box & Whisker Plots:	Values outside of approximately 2.5 interquartile ranges are identified for further review.
Correlation Coefficients:	A correlation matrix (SAS PROC CORR) is produced for each data set. Residual analysis is performed on each pair of variables with Spearman correlation coefficients of approximately 0.75 or greater.
Residual Analysis:	Each pair of variables identified in the above step is analyzed using the STUDENT option in the SAS PROC Reg procedure. Values which are outside of approximately 3 studentized or standardized residuals are identified for review. Attention is given to leverage points using Cook's D statistic.
Graphical Analysis:	Stem and leaf diagrams, box and whisker plots (SAS, 1984), trilinear diagrams (Fetter, 1980 or Hem, 1970), three dimensional graphs, residual plots, time series plots may all be used in reviewing the data during the validation process.

Finally, the cooperator is provided a list of the validation results for questions or comments. Upon mutual agreement, the results of validation are provided to the data manager for inclusion in the final ERL-C data base.

The Final Data Set

The results of validation appear in the final data set as:

1. Validation flags,
2. Entry-specific comments, or
3. Global comments.

These are discussed in some detail below.

Validation Flags --

For the project we have defined five types of validation flags that denote the quality of the data as based on the above discussions. Validation flags are different from other flags used in the data set. A Data Dictionary has been written describing the location and use of flags. The data are qualified with the following validation flags:

Flag	Meaning
# -	The data associated with this flag have not been validated. This is used as a temporary flag to denote such data and is changed upon validation.
? -	The data associated with this flag are suspect. Although this sample may be an outlier, not enough information was available to confirm or deny this value.
X -	These data are rejected and are not supplied to the cooperators. They are archived at ERL-C as a part of the project database.
* -	An asterisk is associated with a "global" comment (discussed below).
-	Values which have no flag have been accepted as a result of validation. These values may still have data quality flags in the associated flag file.

Comments --

There are two types of comments that may be associated with the data. Comments are entry-specific (i.e., relating to a specific value in the database) or "global". The latter refers to a general comment that is included in the final data set and denotes an incident which could affect data quality for more than one sample. Such examples of global comments are analytical methods changes, personnel changes and changes in sampling procedures.

The suspect data flag (?) is applied somewhat subjectively to data of questionable quality. These data may not be statistically different enough to deserve rejection, but there is some reason that the value flagged is suspect. This suspicion may result from statistical tests, the QC data, the historical data, other analytes within the same sample or other indicators of data quality. The option is left to the end-user on how to best use these data, with the understanding that questions remain regarding their quality.

SECTION 5

PERFORMANCE AND SYSTEM AUDIT PROGRAMS

PERFORMANCE AUDIT PROGRAM

Four sources of performance audit samples are being used in the WMP. Performance audit samples are used to evaluate analytical precision and accuracy, and for interlaboratory comparisons. The degree of participation by WMP laboratories in a given program is determined by the parameters and sample types being analyzed. Performance-audit sample procedures for each Task are listed in the individual Task plans (Appendix C).

Environmental Monitoring System Laboratory-Las Vegas Performance Audit Program

EMSL-LV performance audit samples are synthetic solution samples distributed quarterly to participating laboratories. One concentration of a given analyte is prepared each quarter. Data resulting from audit sample analyses are used to assess: (1) intralaboratory precision and accuracy, (2) interlaboratory precision and accuracy, and (3) trends through time. For each analyte, laboratories are requested to perform analyses in triplicate with each replicate measured under different calibrations. Precision calculated from these data includes a component of among-batch variability. Analyte concentrations in each audit sample batch are verified by the EMSL-LV laboratory prior to shipment via overnight express. Concentrations were chosen to represent characteristic stream chemistry values at BBWM. Reports on laboratory performance are provided to each cooperator on a quarterly basis. Annual synthesis reports document performance over time.

Long Range Transport of Air Pollutants

The Canadian Center for Inland Waters (Environment Canada, Burlington, Ontario) conducts an interlaboratory comparisons program as part of the Long Range Transport of Air Pollutants (LRTAP) program. Participating laboratories are sent ten samples of low ionic strength natural waters three times per year. Although replicate analyses may be performed, only one result per analyte per sample is submitted to LRTAP. Nonparametric (ranking) techniques are used to indicate bias. This is a large

program with over 40 participating laboratories in Canada and the U.S. Through a recent agreement with the Canadian Center, the WMP laboratories now receiving the natural samples include the Maine Site and the Aluminum Task group.

EPA Acid Rain Performance Evaluation Program

Only the Maine Site laboratory participates in this program. The program is coordinated by EPA-Research Triangle Park (RTP) for precipitation sampling by National Acid Deposition Program (NADP) affiliated analytical laboratories. Low-ionic strength audit samples are supplied. Parameters include cations, anions, pH, and conductivity. Reports are sent to participating laboratories after data from each round of samples are analyzed.

Soil Exchange Programs

In 1987 an International Interlaboratory Comparisons Study for Soils was conducted for the DDRP by EMSL-LV and the University of Nevada at Las Vegas, Environmental Research Center. Four WMP laboratories participated in the study in which eight soil samples were sent out two times to just under 20 soil laboratories across the U.S. and Canada. Because laboratories used either DDRP methods or methods of their choice, technique comparisons were possible from the study. In addition, bias assessments over a range of concentrations were possible. WMP laboratories may be required to participate in additional comparison studies throughout the duration of the project.

SYSTEM AUDIT PROGRAM

EPA and Technical Support QA staff perform on-site system audits of the field teams and analytical laboratories at random times during the course of the program. On-site audits during sampling and analytical activities are conducted to ensure that protocols are being followed properly, that the laboratory facilities, personnel and equipment are capable of continued operations, and that problems are being identified and resolved quickly.

SECTION 6

MAINE SITE QUALITY ASSURANCE PLAN

The primary group responsible for field sampling and analyses at the Bear Brook site is the Maine Site Team. Because of the pivotal importance of this group, QA/QC for the Maine Site is discussed below.

Principal Investigator responsibilities for major aspects and topics of the research are as follows:

Streams, Hydrology, Groundwater, and Precipitation	Norton, Kahl
Throughfall	Fernandez
Soil Chemistry	Fernandez
Soil Solution Chemistry	Fernandez
Whole Watershed Manipulation	Norton
External Plot Experiment	Fernandez
Laboratory Analytics	Kahl
Permits and State Contracts	Kahl

The Laboratory Manager and Field Coordinator assist the University of Maine Principal Investigators with routine operations, and oversee the daily schedule of other employees. The data and QA/QC Coordinator oversees data handling and QA reports.

ORGANIZATION AND RESPONSIBILITIES OF THE MAINE SITE TEAM

The Maine Site Team consists of researchers from the University of Maine, the U.S. Geological Survey (USGS), and the U.S. Fish and Wildlife Service (Table 15).

TABLE 15. WMP PERSONNEL OF THE MAINE SITE TEAM

Title	Name	Affiliation
Principal Investigator	Stephen A. Norton	Dept. of Geological Sciences
Co-Principal Investigator	Ivan Fernandez	Dept. of Plant & Soil Sciences
Co-Principal Investigator	Jeffrey S. Kahl	Dept. of Geological Sciences
Co-Principal Investigator	Terry Haines	U.S. Fish & Wildlife Service
Hydrologist	Derrill Cowing	U.S. Geological Survey
Hydrologist	Rick Fontaine	U.S. Geological Survey
Scientist	Lindsey Rustad	Dept. of Plant & Soil Sciences,
Computer Sciences Specialist	John Scofield	Dept. of Geological Sciences
Statistician	William Halteman	Dept. of Mathematics

The Laboratory Manager is responsible for assuring the quality and completeness of all chemical analyses on water samples and soil extracts. The responsibilities of the Manager, chemists and technicians are listed below.

The Laboratory Manager:

- Reviews laboratory notebooks, instrument performance records, and data on a regular basis;
- Assures that QA protocols are followed;
- Assists in correcting problems in the laboratory; and
- Reports progress and problems in the laboratory to the Principal Investigators, including summaries of internal QC data.

Laboratory chemists and technicians:

- Conduct analyses under defined QA protocols;
- Maintain appropriate notebooks, instrument logs, and QA records;
- Record observed events that may affect data;
- Report problems or concerns to the Laboratory Manager; and
- Perform routine maintenance on instruments.

Field technicians:

- Collect samples and maintain instruments using appropriate QA protocols;
- Maintain appropriate field notes, instrument logs, and QA records;
- Report significant events or problems with procedures or equipment to the Principal Investigators; and
- Perform routine maintenance on equipment.

The USGS, through a subcontract with the University of Maine, maintains hydrologic gauges at the field site. USGS hydrologists perform routine QA checks on the equipment and report major problems to the Maine Principal Investigators. The agency provides provisional discharge data to the Maine Principal

Investigators on a bimonthly basis. After a review of the data by the agency and the Maine Principal Investigators the USGS provides finalized discharge records to the Maine Principal Investigators for delivery to ERL-C.

SAMPLING PROTOCOL

Glass and Plastic Ware Preparation

All plasticware involved in sample collection are high density linear polyethylene (HDLP). Acid-washing entails: (1) soaking or rinsing articles in 10 percent solution of hydrochloric acid, (2) rinsing at least twice with tap water, (3) rinsing at least three times with water of a conductivity less than 10 $\mu\text{S}/\text{cm}$, and (4) rinsing at least twice with water of a conductivity less than 2 $\mu\text{S}/\text{cm}$ (Nanopure). Glass containers are allowed to drain dry and are then sealed with parafilm. Plastic bottles are allowed to drain and then stored one-third full with deionized water. As plastic bottles are selected for use, the conductivity of the water in one-third of the bottles is checked; any bottles that contain water with a conductivity greater than 3 $\mu\text{S}/\text{cm}$ are rerinsed before use. Also conductivities are checked on all pH syringes, and all meteorologic station buckets.

Sample Collection

At the research site, studies are conducted on both plot and watershed scales. The types and frequencies of sample collections are listed in Tables 3, 4, 5, and 6; types and frequencies of field data are listed in Table 16.

Stream Sampling –

Each stream is sampled at approximately weekly intervals above its respective hydrologic gauging station and as is appropriate in response to discharge along elevational gradients. ISCO automated samplers collect samples as often as hourly during hydrologic events. Table 17 summarizes collection containers and aliquot treatments for stream sampling. An aliquot of distilled water from a subset of sample

TABLE 16. TYPES AND COLLECTION FREQUENCIES OF FIELD DATA

Sampling Level	Class of Data	Data Type	Collection Frequency	Methodology
Watershed	Stream	Discharge output	5 minutes record	Recording stream gauge
Watershed	Precipitation	Wet deposition input	Hourly record	Recording gauge
Plot	Water	Water table	Monthly record	Piezometer wells

TABLE 17. STREAM SAMPLE ALIQUOTS (WEEKLY UNLESS SPECIFIED OTHERWISE)

Container	Parameter
250 ml & 60 ml (Syracuse)	Total aluminum, fluoride
500 ml #1 (Maine)	ANC, specific conductance, color
500 ml #2 (Maine)	Exchangeable, total aluminum DOC Base cations, Si Anions NH ₄ ⁺
500 ml #3 (Maine)	Aerated pH
40 ml DIC glass bottle, septum-capped (Maine)	DIC
60 ml syringe (Maine)	Closed cell pH
Monthly 500 ml #4 & #5 EB3, WB3 sites only (Illinois)	DOC - speciated
Biweekly 500 ml #6 & #7 EB3, WB3 sites only (Syracuse)	Sulfur - isotopes

containers is composited into one bottle to generate the field blank sample. Each container is rinsed copiously with streamwater, filled completely (underwater, if possible) and closed tightly. All bottles are placed on ice as soon as possible. One replicate set of samples is collected from one different sampling station (determined a priori) on each sampling round. The field crew is supplied with labelled sample bottles specifying the stations from which routine and replicated samples should be collected. Sample preservation, storage conditions, and holding times are listed in Table 12.

Precipitation Sampling –

Precipitation samples are collected based upon National Acid Deposition Program (NADP) protocols. If the collectors contain solution, the sample is poured into HDLP plastic bottles, placed in a cooler, and transported to the laboratory. If the collectors contain snow, the bucket is transported to the laboratory where it will be melted. In either case, the total volume of precipitation is collected and measured. If volume is limited, analytical priorities will follow Table 18. For additional details regarding precipitation sampling protocol and QA see Appendix B.

Throughfall and Stemflow Sampling –

Throughfall and stemflow collectors will be sampled weekly. Samples from collectors at each plot will be bulked after the volume (or mass) collected by each one is determined. If bulked sample volumes are insufficient for complete analyses, then analytical priorities will follow Table 19.

Lysimeter Sampling –

Tension lysimeter samples are collected biweekly and zero-tension lysimeter samples are collected monthly during the snow-free season. Samples from both lysimeter types are collected on a monthly basis during the winter, or as conditions permit. Samples from replicate lysimeters at each plot are bulked by depth after the volume collected for each one is determined. If bulked sample volumes are insufficient for complete analyses, then analytical priorities follow Table 19.

TABLE 18. MAXIMUM CONTROL LIMITS FOR INTERNAL QUALITY CONTROL: MAINE SITE

Parameter	Max. Percent Difference From Theoretical Concentration of the Reference Material
Al-total	15%, $\pm 0.4 \mu\text{moles/L}^{-1}$
Ca ²⁺	5%, $\pm 5.0 \mu\text{eq L}^{-1}$
Mg ²⁺	5%, $\pm 8.2 \mu\text{eq L}^{-1}$
Na ⁺	5%, $\pm 4.4 \mu\text{eq L}^{-1}$
K ⁺	5%, $\pm 2.6 \mu\text{eq L}^{-1}$
Cl ⁻	7%, $\pm 5.0 \mu\text{eq L}^{-1}$
NO ₃ ⁻	7%, $\pm 5.0 \mu\text{eq L}^{-1}$
SO ₄ ²⁻	7%, $\pm 5.0 \mu\text{eq L}^{-1}$
NH ₄ ⁺	10%, $\pm 11.1 \mu\text{eq L}^{-1}$
DIC	10%, $\pm 34 \mu\text{moles L}^{-1}$
DOC	10%, $\pm 34 \mu\text{moles L}^{-1}$
Si	10%, $\pm 14 \mu\text{moles L}^{-1}$
Conductivity	10%, $\pm 2 \mu\text{S cm}$
ANC	7%, $\pm 5.0 \mu\text{eq L}^{-1}$
pH	0.1 standard units

**TABLE 19. PRIORITY OF ANALYSES FOR VOLUME - LIMITED SAMPLES
(SOIL LYSIMETERS, THROUGHFALL, PRECIPITATION, SNOW MELT,
STEMFLOW, AND PIEZOMETERS)**

Priority	Parameter
1	Anions
2	Cations and Aluminum
3	pH
4	Silica
5	Specific conductance
6	DOC*
7	Acid neutralizing capacity

*Not applicable to all sample types.

Snow Lysimeter Sampling –

Six high elevation (four in softwood; two in hardwood) and two low elevation (both in hardwood) snowmelt lysimeters are located within the paired catchments. All four hardwood snow lysimeters are equipped with tipping bucket gauges connected to data loggers for continuous monitoring of snowmelt events. Snowmelt samples are collected weekly when significant melt is observed. Analytical priorities follow Table 19.

Piezometer Wells –

Groundwater samples from the piezometer wells are collected monthly. Prior to collection, either three well volumes of solution or all the solution (whichever comes first) are removed from each well. The well is then allowed to recharge, and samples are taken as soon as volume permits. Analytical priorities follow Table 19.

Soil Air Sampling –

Soil air samples are collected monthly from the external and reference plot soil air tubes. Samples are withdrawn with a syringe, stored in a vacuum bottle, and shipped immediately to the University of Illinois for analysis.

Buried Soil Bag Retrieval –

Three buried soil bags are removed from each of the external and reference plots on an annual basis. The 5 cm of the B horizon immediately below each buried bag is also removed for analysis. All samples are transported immediately to Syracuse for freeze drying and shipment to the appropriate Tasks for analysis.

Soil Sampling –

Soil sampling from external plots, reference plots, and benchmark pits was completed in 1987-1988. Sampling methods and QA can be found in Appendix A.

MONITORING OF FIELD EQUIPMENT

Technicians check the operation of field equipment on a weekly basis. All equipment problems are reported to the Principal Investigator and/or Field Coordinator. The operating conditions of all equipment, any difficulties encountered, and actions taken to correct equipment problems are recorded in field notebooks. Notebooks include the nature of the activity, date, and initials of the technician responsible.

Precipitation Gauges

Belfort recording precipitation gauges are calibrated biannually using a standard weight set provided by the manufacturer. The operation of the watch mechanism and condition of the antifreeze mixture is checked weekly. The antifreeze solution is replenished as necessary.

Wet/Dry Collectors

The operation of each wet/dry collector is checked weekly. As part of this routine check, the sensitivity of the moisture sensor is assessed, the sensor is cleaned with distilled water, and the collection bucket is replaced.

Stream Gauges

University of Maine technicians visit the stream gauges each week to check the functioning of equipment and to clear the devices of any debris or ice that could affect their operation. Any problems detected are reported to the Maine Principal Investigators and the USGS. Stream gauges are also visited approximately monthly by USGS personnel who collect records and service the recording instruments and structural features of the equipment. Stage-discharge relationships have been calculated for each stream for conversion of stage data to discharge. Rating curve calibrations use concurrent field determinations of stage and discharge made by USGS and University of Maine personnel. Redundant methods of determining discharge are used, to ensure data completeness. University of Maine technicians have installed pressure

sensors within the stilling wells that are calibrated to monitor discharge. These serve as a backup to the potentiometers installed by the USGS.

Lysimeters

Lysimeters are visited weekly on a regular schedule (Table 3) by University of Maine technicians who check the functioning of suction devices on tension lysimeters and for the occurrence of leaks in the lysimeter systems. Any problems encountered with soil solution collectors are recorded and reported to the Maine Pls.

Snow Lysimeters

Prior to their installation all devices were acid-washed and checked for leaks. Any problems observed in the field with the flow of meltwater to collection bottles are corrected and reported.

Throughfall Collectors

Prior to their installation all collectors were acid-washed and checked for leaks. Throughfall collectors are visited weekly by University of Maine technicians who check for leaks and remove debris from the collectors. Sample collection bottles are replaced with clean bottles, and parts that remain in place (funnels, tubing, etc.) are thoroughly rinsed with deionized water.

Soil Air Samplers

Samplers are checked monthly for ease of collection and collection tube caps are inspected. If the tubes appear blocked or clogged, the samplers are replaced.

Litterfall Collectors

Collection traps are cleaned with deionized water before placement in the field. Traps are inspected biweekly for evidence of damage or disruption by animals.

MONITORING OF SAMPLING PROCEDURES

The Maine PIs make monthly on-site inspections of sampling procedures of each field technician for each type of sample collected (i.e., stream water, lysimeter solutions, precipitation, throughfall). During these visits, the PIs review proper sampling procedures as needed with field technicians, and record findings and actions in a standard form field notebook designated for evaluation of field technician performances.

SAMPLE PREPARATION

Field Solutions

Samples for pH, ANC, DIC, specific conductance, and apparent color are not filtered for Maine Site analyses. Other analyses in the Maine Site laboratory are performed on filtered subsamples, using 0.4 μm nucleopore filters for all parameters except DOC. DOC aliquots are filtered through 0.7 G/F glass fiber filters.

Filter Protocol –

Vacuum filtration with a plastic magnetic filter apparatus and collection flask is used. New filters are rinsed first with 50-100 ml distilled water, then 10-20 ml of sample. These rinses also serve to rinse the collection flask. A new filter is used for each sample; several filters are sometimes necessary to obtain sufficient volume for analyses for especially DOC-rich samples. Each new filter is rinsed with distilled water and sample before use.

DOC and true color subsamples are filtered through glass fiber filters with a baked Millipore glass filter apparatus. All apparatus are wrapped in aluminum foil and baked at 400°F for 3 hours.

Sample Preservation –

The cation, aluminum and silica subsamples are acidified with nitric acid to give a sample acid concentration of 1.25 percent (v/v). Sulfuric acid is used in DOC aliquots. All samples and aliquots are refrigerated until analysis.

SAMPLE CUSTODY

Sample Identification Codes

All samples are uniquely labelled with an 18-character code which contains the date and time of collection, the sample type (stream, throughfall, soil lysimeter etc.), the sample ID, and the sample record type (routine, standard, duplicate, etc.). An example is '0122871315SWB1--1', where '012287' and '1315' are the date and time of collection, 'S' is the sample type (stream), 'WB1--' is the sample ID and '-1' is the record type.

Sample Tracking

A data management system for the WMP has been written in FOXBASE, a dBASE III + compatible language, for a personal computer running MS DOS. The system is designed to:

- Track field collections;

- Determine and generate the number and type of laboratory QA/QC samples required per sample batch;

- Generate field collection and laboratory data entry sheets;

- Record and track laboratory raw data and input flags;

- Calculate by batch, laboratory precision and accuracy;

- Identify holding time violations;

- Identify blank contaminations;

- Flag data quality objective violations by parameter and/or batch;

- Track and flag sample reruns;

- Identify and track data validation flags and comments;

- Generate tables of accuracy, precision, blanks by parameter and sample type;

- Generate ASCII files for data distribution.

Initial sample data information is entered by an appointed laboratory technician soon after the samples arrive from the field. For a particular sample type the operator enters into the database system the date,

time, and location of collection, the volume collected where appropriate, and other pertinent information. This information is used to generate the unique 18-character identification code for each sample and is stored in an appropriate database file. Based on the number of samples collected, codes for an appropriate number of QA/QC samples (e.g., spikes, standards, blanks, etc.) are also generated. These, along with the codes of the samples collected are stored within individual parameter files (cations, anions, pH, etc.). Next, laboratory data sheets, which list all samples to be analyzed for a particular group of parameters (e.g., cations, anions, etc.) are printed and distributed to laboratory personnel. The laboratory technicians use the form as a guide to identify which samples are run and as a template to record analytical results.

The completed laboratory data sheets are turned into the laboratory QA/QC inspector who performs an initial evaluation. At that time, he or she may request that a sample be re-analyzed. Once the QA/QC inspector is satisfied, the forms are given to a data-entry person who enters the raw data into the system via screen templates designed to resemble the laboratory data sheets. All data are printed out and compared to the original data forms to identify typographical errors that occurred during data entry.

The complete, typo-checked data set is then processed by a routine which calculates precision and accuracy of QA/QC samples, and identifies blank contamination problems and holding time violations. Results from these calculations are stored for inclusion in quality assurance reports. Samples that violate a data quality objective are flagged as such within the database and may be re-analyzed, if requested by the QA/QC inspector. Tables of precision, accuracy, blanks, and routine chemistry are produced for each sample type.

Next, charge balance, ion routines, and other chemical relationships that aid in identifying outliers are calculated. These results are examined by the QA/QC inspector who decides whether a validation flag should be placed on any questionable samples and what that flag should state. He or she may also request that a sample be reanalyzed at this step. If validation flags are generated, they are entered into an appropriate database file.

Sample Shipment

After the Maine laboratory has completed filtering and subsampling for cations, anions, NH_4/Si , and aluminum (for Syracuse and Maine); and after pH, acid neutralizing capacity (ANC), conductivity, and color analyses are completed, the lab prepares a form containing initial sample volume information. Subsamples are archived, and the remainder of the sample is weighed. Samples are then bulked and shipped to the task groups as appropriate. Copies of the sample shipment information and the laboratory sample volume datasheets are maintained by the laboratory.

All solution samples to be shipped are bottled in acid-washed HDLP containers. Samples are labelled and a description of any processing (i.e., filtering, screen mesh size, drying) that the sample has undergone at the University of Maine are clearly marked with indelible ink on both the lid and the side of each container. Two copies of an invoice sheet listing each sample in the shipment are included in the package. One copy of the invoice will be retained by the recipient; the other is signed and returned to Maine where it will be checked against the original invoice. Samples are shipped by United Parcel Service. A log of requests for, shipments of, and receipts of samples will be maintained by Maine and checked regularly.

ANALYTICAL PROCEDURES

The parameters of solid soil that are measured by various task and site investigators, and the methods are listed in Table 5. Table 4 lists measurements and methods for the analysis of field solutions (precipitation, throughfall, snowmelt, stream, stemflow and lysimeter water) by the Maine Site Laboratory.

CALIBRATION PROCEDURES

Calibration standards are prepared from American Chemical Society (ACS) grade reagents or from commercially available instrumental standards of a certifiable grade. All water used in the preparation of standards meets the specifications of American Society of Testing and Materials (ASTM, 1984) Type 1.

Atomic Absorption Spectrophotometer, Ion Chromatograph, Infrared Absorptiometer, Automated Colorimetric Analyses

Standards –

The above instruments are calibrated for each analyte by analyzing a reagent blank and a number of standards that bracket the expected sample concentration and fall within a linear range. If appropriate instrument-based software is not available, a calibration curve is drawn for each analyte by plotting peak height or absorption against the standard concentration.

Initial Calibrations –

The correlation coefficient of the linear dynamic range (LDR) for each analytical technique is established based on a run of analytical standards. If the sample concentration is above the range of calibration standards used, analyses are repeated using either a higher concentration standard or lower concentration samples. If sample concentrations fall below the range of calibration standards and above the specified detection limit, then a lower concentration calibration standard is used.

Recalibrations –

An unacceptable value (Table 18) for reference material or calibration standards requires the recalibration of the instrument along with the reanalysis of all samples subsequent to the last acceptable reference material or calibration standard value. If further unacceptable values are produced, all analyses cease and the Laboratory Manager is notified. Analyses proceed when the Laboratory Manager is satisfied that the equipment is functioning properly and quality assurance objectives are being achieved.

Calibration Blanks –

Calibration blanks are run immediately after the preliminary calibration, during the run, and at the end of the run, to detect any baseline drift.

pH Electrodes for Meters and Automatic Titrators

Electrodes for pH measurement are stored in distilled water or the solution recommended by the manufacturer when not in use. The electrode is calibrated using a 2 point (pH 4 and pH 7) calibration technique. If an electrode response slope less than 98 percent is obtained, that electrode is not used. Electrode performance in low ionic strength water is verified daily by analysis of dilute standardized acid prepared from a dilution of titration acid, and by analysis of standard air-equilibrated distilled water.

Automatic Acid Neutralizing Capacity Titrator

ANC titrations use acid that has been standardized against a standard base, which in turn has been standardized against a primary standard of potassium hydrogen phthalate. A blank and standard are run in each batch of 18 samples on the Radiometer ARAS™.

Conductivity Meter

The conductivity meter has its correction factor checked every 2 weeks by measuring the conductivity of a traceable conductivity standard at 25°C.

Color

Color is determined spectrophotometrically at a wavelength of 460 nm in a 10 cm cell. A calibration curve is drawn by plotting the absorbance of a range of traceable PtCo color standards.

PREVENTATIVE MAINTENANCE

All pieces of major laboratory equipment are periodically serviced by factory service personnel. In addition, the following maintenance is carried out by laboratory personnel according to the time scale noted.

Atomic Absorption Spectrophotometer

The burner chamber and head is cleaned and the burner head is washed at least weekly in distilled water. The windows in the burner compartment are carefully cleaned with lens tissue as needed.

Ion Chromatograph

The Ion Chromatograph is checked for leaks and crimps on a daily basis. Lubrication of pumps and autosampler is carried out according to the manufacturer's schedule. The conductivity detector is cleaned and calibrated at least every 6 months using recommended techniques. Bed supports are replaced approximately every month. Columns are cleaned at least once a month. The cleaning frequency depends on the type and volume of sample throughput.

Auto Analyzer

Peristaltic pump tubing is replaced on an as-needed basis or after 250 hours of use. Pump platens, colorimeter lamp, and interference filters are changed approximately yearly.

INTERNAL QC CHECKS AND CORRECTIVE ACTION

QC samples and/or blanks are introduced during sample collection, sample collection, sample preparation, and sample analysis to assess precision and accuracy at specific stages in the experimental process. The type and frequency of QC samples obtained during each stage are listed in Table 20.

Sample Collection

One collocated sample is taken from one stream sampling station per stream sampling round. The station from which the collocated sample is taken is different on each sampling round. Laboratory splits are generated for throughfall, lysimeters, snowmelt, stemflow and piezometer samples, when volume is sufficient, at a rate of 10 percent. Field blanks are generated as described in Table 20. A field blank is a sample bottle that has been filled in the field with distilled water discarded from sample collection bottles and subjected to the same analyses as a water sample.

TABLE 20. TYPES AND COLLECTION FREQUENCIES OF FIELD SOLUTION QUALITY CONTROL SAMPLES

Check ¹	Sample Flow Point	Sample Type	Frequency ²
P	Collection	Collocated	1/stream sampling event
P	Post bulking	Laboratory splits	1/collection event or 10% of all lysimeter throughfall, stemflow, and piezometer samples collected when volume allows
C	Collection	Field blank	1/sampling event for streams, lysimeters, and piezometers; 1/month for precipitation collectors
P	Analysis	Analysis replicated	5% of all analyses for which sample is available
A	Analysis	Analysis matrix spike	1/field batch for anions, cations, Al, NH ₄ , Si
C	Analysis	Analysis blank	1/analytical run (at least)
A,P	Preparation of material	Reference	Quarterly or when supply is low
A,P	Interlaboratory	Comparison	Determined by EPA
A,P	Analysis	Internal quality control check	Approximately 5% of samples analyzed
A,P	Analysis	External quality control check	1/calibration (internal standards only for conductivity and color)

¹ A = accuracy

P = precision

C = contamination

² Frequencies are based on the number of routine samples collected.

Sample Preparation

To check for accuracy during sample preparation and analysis, reference samples containing appropriate analytes at concentrations simulating those of natural streamwater are prepared for species for which external reference standards are available. These reference samples are prepared and analyzed using the same methods as the regular samples. Duplicate reference samples are used to check for precision.

Sample Analysis

Calibration standards are prepared from ACS grade reagents or commercially available instrumental standards of a certifiable grade. These standards are included in every analytical run. Distilled water used for standards will meet the specifications of ASTM (1984) Type 1 water. The following QC samples are analyzed using the same techniques as the regular samples. Analysis of replicate samples are performed on 5 percent of all samples for which volume is sufficient. One laboratory matrix spike is analyzed with each field batch, when volume permits, for anions, cations, NH_4 , Si, Al. The volume of the spike added is less than 1/1000 of the sample volume, and the concentration of the spiked analyte is approximately equal to the ambient analyte concentration. An analysis blank consisting of distilled water collected just prior to analysis is also analyzed with every analytical batch. Reference material containing analyte concentrations representative of a typical sample are analyzed during each analytical run. The reference material is prepared independently of the calibration standards and may consist of independently analyzed material.

Corrective Action

Blank Samples –

In all cases, the measured analyte in blank samples should be less than twice the detection limit for the analyte under investigation. "High" blanks (more than twice the detection limit) are regarded as evidence of contamination and all relevant samples are reprocessed when possible, or flagged in the database whichever is appropriate after the source of contamination is identified and eliminated. Blank data are submitted with sample data to EPA.

Matrix Spike Recovery –

Matrix spike percent recovery from the laboratory matrix spike samples is evaluated by calculating percent difference. Recovery is expected to be within the accuracy DQOs for the analyte. If this is not achieved, the spiked sample is flagged in the database. If a problem occurs, the spike stock is evaluated using distilled water spikes.

Replicate Sample Comparisons –

"Between-duplicate relative standard deviations" for field and laboratory replicate samples are calculated and should fall inside of the limits presented in Table 9. Precision problems are solved by the analyst when possible. All such problems are included in the QA reports.

PERFORMANCE AND SYSTEM AUDITS

Performance Audits

The WMP Performance Audit Program provides blind audit samples on a quarterly basis for the following parameters: ANC, anions, cations, DOC, DIC, NH_4 , pH, conductivity, Si, and true color. In addition, the EPA Acid Rain performance audit sample program provides low ionic strength samples semiannually. Also, LRTAP audit samples from natural sources are provided three times annually.

System Audits

EPA technical support QA staff perform system audits of field teams and the analytical laboratory at least annually.

DATA REDUCTION, VALIDATION, AND REPORTING

Data Reduction/Screening

The data management system produces tables and flags to document the quality of data. Data are screened for: holding times, blank values, precision, accuracy, and completeness.

After all analyses for a given sample lot have been completed, charge balance and conductance balance are calculated (Hillman et al., 1986). Problem data discovered by the screening program or a reviewer are dealt with as follows. If there is enough of the sample remaining and holding times have not been exceeded, the analysis is rerun and the new results go through the screening process from the beginning. If the analysis cannot be rerun, a decision is made to flag, comment on, or reject the value. Rejected data is permanently stored in a separate data set and original values are sent to ERL-C for purposes of review. The system generates summaries of all quality assurance data. Prompt recognition of problems is assured by screening by individual analysts and QA/QC officers during or soon after each run completion.

Data Security

Data is stored both on standardized dataforms and on "Winchester" computer drives. Back-up files on floppy disks are updated regularly. Completed data sets are reviewed by the QA Officer and the Maine Principal Investigators. Reviewed data is made available to the EPA in the form of text files on floppy disks.

SECTION 7

QUALITY ASSURANCE REPORTS TO MANAGEMENT

Reports from the Maine Site Team and all Tasks are submitted on a quarterly basis to the EPA group at ERL-C. These reports contain QA/QC data from the individual laboratories demonstrating that they are meeting their respective QA/QC goals regarding accuracy and precision as listed in the individual Task QA plans (Appendix C) and Tables 9 and 10 for all applicable parameters. All WMP laboratories maintain running summaries of their respective QC data by QC sample type (e.g., laboratory replicates, field duplicates, calibration checks, etc.) on an analytical run (batch) basis. The use of control charts is highly recommended for this. Task laboratories, in their quarterly QA reports, should present the percent (and total number of samples this represents) of each QC sample type that fell outside of their respective QA goals for the quarter and parameter(s) evaluated. A tabular format should be adequate for this purpose for the Task laboratories. Explanations and corrective action(s) associated with the out-of-limit QC data are included in the quarterly reports to ensure documentation of any problems for future data users.

The Maine Site Team laboratory, due to its sample load, uses control charts to maintain a running summary of QC data and to document analytical quality through time. Quarterly QA reports from the Maine Site Team to ERL-C include copies of these control charts for the previous 3 months and QA reports generated from the database management system. Deviations from the Maine Site QA goals during the quarter are discussed in the reports and corrective action documented.

Performance audit sample results (e.g., from the quarterly synthetic solution samples) are sent to ERL-C as these analyses are completed by the respective laboratories. WMP laboratories also need to evaluate results from all performance evaluation studies which they currently participate in, and need to comment on discrepancies, concurrences, and any corrective action taken.

SECTION 8
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SECTION 9

ACRONYMS

AAS	Atomic Absorption Spectrophotometer
ACS	American Chemical Society
AERP	Aquatic Effects Research Program
ANC	Acid Neutralizing Capacity
ASRL-RTP	Atmospheric Sciences Research Laboratory-Research Triangle Park
ASTM	American Society of Testing and Materials
BBWM	Bear Brook Watershed in Maine
CEC	Cation Exchange Capacity
CV	Coefficient of Variation
DDRP	Direct/Delayed Response Project
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DQO	Data Quality Objective
EMSL-LV	Environmental Monitoring Systems Laboratory-Las Vegas
EPA	Environmental Protection Agency
ERL-C	Environmental Research Laboratory-Corvallis
FRP	Forest Response Program
HDLP	High Density *****
IC	Ion Chromatograph
ICP	Inductively Coupled Plasma Emission Spectrometer
IRS	Irrigation System (on external plots)
LDR	Linear Dynamic Range
NADP	National Acid Deposition Program
NBS	National Bureau of Standards
NSWS	National Surface Water Survey
PCU	Platinum Cobalt Units
PI	Principal Investigator
QC	Quality Control
QA	Quality Assurance
QAMS	Quality Assurance
RSD	Relative Standard Deviation
SCS	Soil Conservation Service
SUNY	State University of New York
SSI	Size Selective Inlet
USDA	United States Department of Agriculture
USGS	United States Geological Survey
WMP	Watershed Manipulation Project
ZTL	Zero Tension Lysimeter

Appendix A

**PREPARATION AND QUALITY ASSURANCE OF SOIL SAMPLES
FOR BENCHMARK PIT CHARACTERIZATION**

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1. PREPARATION OF SOIL SAMPLES FOR BENCHMARK PIT CHARACTERIZATION

SAMPLE HANDLING AND STORAGE

It is important to avoid storing soil samples at excessively warm temperatures to keep microbial activities at a minimum. Samples must be stored at 4°C within 24 hours of sampling unless they are immediately laid out to dry. Soil samples that are air-dry do not have to be refrigerated, but care should be taken that samples are not exposed to extreme temperatures or any sources of contamination. "Moist" samples (i.e., samples that are not dried before being analyzed) are to remain refrigerated until shipped.

SAMPLE TYPES AND LABELING

Routine samples, sieve-analysis samples, moist samples, field duplicate and volume-replacement samples will be taken during sampling. Routine samples consist of approximately 1/2 gallon of material collected in a single bag that passes a 20-mm sieve; 3/4 of a gallon of soil will be collected for all organic horizons. (The labelling instructions below allow for the case when 2 bags are necessary to compensate for a high rock fragment content (over 45%) of the <20 mm sample).

Sieve-analysis samples are samples taken from the entire volume of B and C horizons. Field samples for sieve-analysis must yield at least 500 grams (dry wet) of < 2 mm material. Moist samples will be collected for every horizon that routine samples are taken from. They will be sieved with a 20 mm sieve and then sent to the designated lab without being dried or prepared. Moist-samples taken in the field must yield at least 350 grams (wet weight) of < 2 mm.

A single field duplicate will be taken for routine and moist samples every third pedon sampled, yielding a total of 3 field duplicates for these sample types. Two field duplicates will be taken for sieve samples, one every fourth pedon. These samples are obtained by placing alternate trowelfuls of sample into two different bags. A different type of horizon (different horizon designation) will be sampled each time.

Volume-replacement samples are taken from circular holes, approximately 10-cm diameter, whose volumes are measured with known-volumes of beads. Two samples will be obtained for each horizon where possible.

Each sample will be labeled with the date, horizon designation and horizon depth. A sample code will be included on the labels. The first two letters of the code identifies the sample type - "RS" for routine samples, "RD" for the field duplicate of the routine, "SS" for sieve analysis samples, "SD" for field duplicates of the sieve samples, "MS" for moist samples, "MD" for field duplicates of the moist samples, and "VR" for volume-replacement samples.

The next two digits indicate the pedon number and last two digits (separated from the first two with a dash) indicate the horizon number. The horizon number corresponds to the line number of that horizon as recorded on the 232 Soil Description Form. For example, a routine sample that is from the first WMP benchmark pit, horizon 2, is labeled "RS01-02". Where horizons were combined, both horizon numbers were kept (e.g., RS01-0506). Volume replacement samples are given an additional 2 digit code to indicate a replicate sample; these numbers were placed in front of the pedon number.

DRYING ROUTINE SAMPLES, SIEVE-ANALYSIS SAMPLES, AND FIELD DUPLICATES

Routine sieve-analysis, and field duplicate samples must be dried in an area isolated from possible sources of contamination. Samples will be placed on a sheet of kraft paper that is labeled with the date sampled, the horizon designation and the sample code. An additional piece of kraft paper placed over each sample will help reduce the risk of dust contamination.

The soil should be stirred every other working day to facilitate drying. This should be done with a clean gloved hand or with a tool that is wiped after each soil. Use an unpowdered glove. Any observations of fungal or algal growth in the samples must be noted. For wet samples, the bottom piece of kraft paper may have to be changed often at first.

Record data about air dry moisture on Form 1. To verify that air-dried soils are sufficiently dry, the moisture content must be determined for every horizon for all pedons. Take a sample 15 - 20 g

and weigh it to the nearest 0.01 g, then place it in a preweighed drying dish. Place the dish in a 105°C oven for 24 hours for mineral horizons or in a 60°C oven for organic horizons and then record the final mass. Samples are sufficiently dry when they are less than 2.5% moisture. Organic samples are sufficiently dry if they appear dry and have a steady moisture content for 24 hours. The soil samples are then disaggregated and sieved.

Moist samples will not be dried. They will be put into cold storage (at 4°C) until it is time to ship them. Samples will be collected by ME and shipped to SUNY-Syracuse. Some of these samples will be distributed to cooperators and the rest will be freeze-dried and stored.

DISAGGREGATION AND SIEVING

Routine and sieve-samples with their accompanying field duplicates are disaggregated and then sieved when they are air-dry. The soils in this project may have low enough clay content so that they do not need to be disaggregated. Because this process may be dusty it should be carried out where the dust will not contaminate the other samples.

The entire bulk routine or field duplicate sample must first be weighed. Weigh the sample to 0.01 g and record on the Form 2. Large pieces of stems and roots should be removed before weighing.

To disaggregate spread portions of the sample between sheets of kraft paper. Gently roll the sample with a rolling pin, applying only enough pressure to break up clods - not enough to break up weathered rock fragments.

To sieve, place the sample on a 4.75-mm mesh sieve and gently push the soil through with a rubber stopper. Place the material that does not pass the 4.75-mm onto a 2-mm sieve. Weigh the total rock fragments that do not pass the 4.75mm sieve and record the mass in the '4.75 - 20-mm' space on Form 2. Weigh the rocks that do not pass the 2-mm sieve and record in the '2-4.75mm' space on Form 2. The percent rock fragments will be calculated at Corvallis.

an Erlenmeyer flask, a small piece of cotton cloth or several Kimwipes, a one holed rubber stopper that fits the flask, a piece of glass or plastic tubing, and two lengths of vinyl tubing. Construct as follows:

- Place the cloth or Kimwipes in the flask,
- Connect the side arm of the flask to the air nozzle with a length of vinyl tubing,
- Place the piece of glass or plastic tubing into the rubber stopper,
- Connect a piece of vinyl tubing onto the end of the tubing that is in the stopper,
- Place the stopper into the flask, adjust the air pressure so that it doesn't eject the stopper.

HOMOGENIZATION AND SUBSAMPLING

Sample preparation duplicates are prepared by splitting the field duplicates and the corresponding routine sample after they have been homogenized. The routine samples, field duplicates and prep lab duplicates must be homogenized and split into samples to be sent to other laboratories. The exact sample size to be prepared for each laboratory is presented in Table 1.

A riffle splitter (7 passes) is used to homogenize the samples. The riffle sampler must be cleaned with compressed air between samples using the above described trap.

Pour the less than 2mm material evenly across the baffles of the riffle sampler with the material going into two trays. Repeat five times using the material from a different tray each time. Then transfer the material from both trays onto another tray. Pour this material into the riffle sampler obtaining two samples.

Handling of Routine Samples and Duplicates

Each routine duplicate (RD) and its accompanying routine sample (RS) will weigh approximately 1.5 kg after drying and sieving to $< 2\text{mm}$. Each of these samples should be split in half. One of these halves will be designated as the original sample (either RS or RD), the other becomes the preparation duplicate. Preparation duplicates will be labeled with a P at the end of the sample code.

Send the appropriate amount to recipient labs (Table 1) archiving any remaining material. Archived samples should be stored in the dark away from excessive heat.

Handling of Moist Samples

Each moist sample (MS) and associated field duplicates (MD) needs to be stored cool until shipping. The moist samples should be stirred in the original bag and then split evenly. One set will be shipped and the other set archived (in case reanalysis is necessary) until the analyses are completed. If possible, samples should be shipped in styrofoam coolers with frozen gel-packs.

Handling Sieve-Analysis Samples

Handling is similar to routine samples. After riffle-splitting for homogenization, at least 500 g will be split and sent to the recipient lab, and the remainder of the sample temporarily archived. Preparation duplicates will need to be made from the one field duplicate (SD) and the associated sample (SS), following the procedure for routine samples.

AUDIT SAMPLES

Audit samples arriving from EPA-Las Vegas will be inserted into the packages of samples designated for a given lab according to Table 2. No preparation or special handling will be necessary for audit samples.

SAMPLE TRACKING AND SHIPMENT

Samples will be shipped to receiving labs according to the sample specifications in Table 2.

PROCESSING VOLUME-REPLACEMENT SAMPLES

Volume-replacement samples will be oven dried at 105°C for 24 hours. Samples are allowed to cool for 30 minutes in a dessicator. The sample is then weighed and the mass recorded on Form 3 in

the column OD_WT. The sample is then sieved with a 2-mm sieve and the mass of the rock fragments is determined and recorded to the nearest 0.01g on Form 2 in the column R_FRAG.

The rock fragments from four horizons that contain rock fragments will be used to estimate the particle density of rock fragments for these watersheds. For each of the four horizons take a subset of rock fragments about 300 g. Weigh the rock and record the mass.

The volume will be determined by the water displacement method. Degas about 750 ml of deionized water in a 1 L beaker by boiling it until no rising gas bubbles are observed. Place a watch glass on the beaker and allow to cool to room temperature. Place the beaker on a balance and tare the balance. Record the temperature of the water to the nearest °C. Submerge the rock fragments in the beaker either in a hairnet or nylon netting. Record the mass indicated on the balance. The volume of the rock fragments is:

$$\text{Volume of Rock Fragments} = \frac{\text{Mass after rock submerged}}{\text{Density of Water (at that } ^\circ\text{C)}}$$

A table of the density of water at different temperatures is given in Table 3. The density of each subset is the mass in grams divided by the volume in cm³:

$$\text{Subset particle density} = \frac{\text{Mass of rock fragments}}{\text{Volume of rock fragments}}$$

The estimated particle density of the rock fragments is the sum of the four subset densities divided by 4.

The mass of the material that passes a 2-mm sieve is calculated by:

$$\text{Mass of } < 2\text{-mm} = \text{Total oven-dry sample mass} - \text{mass rock fragments}$$

The volume of rock fragments in each sample is estimated by dividing the mass of the rock fragments by the estimated particle density of the rock fragments.

The final bulk density is calculated by:

$$\text{Bulk Density} = \frac{\text{Mass of } < 2\text{-mm}}{(\text{Volume determined in field with beads} \\ \text{minus volume of rock fragments})}$$

FORMS

FORM 1 - WMP Benchmark SoilsPage of

Air Dry Moisture Determination

* with crucible	A	B	C
-----------------	---	---	---

[illegible]

Page ____ of ____

Mass to 0.01 grams

[illegible]

Page ____ of ____

Calculated Rock Density = _____ g/cm³ Mass to 0.01 grams

[illegible]

TABLE 1. SAMPLE TYPES, RECIPIENTS AND SAMPLE SIZES FOR WMP BENCHMARK PIT SOILS

Sample Type	Recipients	Analyses	Sample Size
Routine Samples (and associated field and prepara- tion duplicates)	Dr. Knute Nadelhoffer Marine Biological Lab Woods Hole, MA 02543	Total carbon Total nitrogen	100 g
	Dr. Myron Mitchell CESF SUNY - Syracuse Syracuse, NY 13210	Total sulfur	100 g
	Dr. Robert Fuller SUNY - Plattsburgh Plattsburgh, NY 12901	pH (H ₂ O) pH (.002 M CaCl ₂) CEC - NH ₄ Cl Extractable bases in NH ₄ Cl (Ca, Mg, Na, K, Mn, Al, Fe) Extractable bases in .002 M CaCl ₂ (Ca, Mg, Na, K, Al) SO ₄ , H ₂ O extractable PO ₄ 6 Pt. Sulfate adsorp- tion isotherms 6 Pt. Sulfate desorp- tion isotherms	150 g
Sieve analysis samples (and associated field duplicates)	Dr. Rich Valentine Dept. of Civil and Environmental Engrg. University of Iowa Iowa City, IA 52242	Particle Size analysis on 20 samples	500 g
Moist samples (and associated field duplicates)	Dr. John Aber Univ. of New Hampshire Durham, NH 03824	Laboratory Incubations for N mineralization	350 g

TABLE 2. EXPECTED NUMBERS OF BENCHMARK SOIL SAMPLES FOR SOIL RECIPIENTS

Nadelhoffer, Mitchell & Fuller

Routine Samples	51 ¹
Field Duplicates	3
Preparation Duplicates	6
Audit samples	<u>3</u>
	63

Aber

Moist Samples	51
Field Duplicates	<u>3</u>
	54

Valentine

Sieve Samples	16 ²
Field Duplicates	1
Preparation Duplicates	2
Audit Samples	<u>2</u>
	20

¹ (8 pedons x 6 samples = 48 samples + 3 samples from a possible ninth pedon)

² (One B and one C sample from each pedon (2 samples x 8 pedons))

TABLE 3. DENSITY* OF WATER

°C	0	1	2	3	4	5	6	7	8	9
0	0.9999	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000	0.9999	0.9999	0.9999
10	0.9997	0.9996	0.9995	0.9994	0.9993	0.9991	0.9990	0.9988	0.9986	0.9984
20	0.9982	0.9980	0.9978	0.9976	0.9973	0.9971	0.9968	0.9965	0.9963	0.9960
30	0.9957	0.9954	0.9951	0.9947	0.9944	0.9941	0.9937	0.9934	0.9930	0.9926
40	0.9922	0.9919	0.9915	0.9911	0.9907	0.9902	0.9898	0.9894	0.9890	0.9885
50	0.9881	0.9876	0.9872	0.9867	0.9862	0.9857	0.9852	0.9848	0.9842	0.9838
60	0.9832	0.9827	0.9822	0.9817	0.9811	0.9806	0.9800	0.9795	0.9789	0.9784
70	0.9778	0.9772	0.9767	0.9761	0.9755	0.9749	0.9743	0.9737	0.9731	0.9724
80	0.9718	0.9712	0.9706	0.9699	0.9693	0.9686	0.9680	0.9673	0.9667	0.9660
90	0.9653	0.9647	0.9640	0.9633	0.9626	0.9619	0.9612	0.9605	0.9598	0.9591

*Also the specific gravity or unit weight of water in grams per milliliter

2. QUALITY ASSURANCE FOR BENCHMARK SOIL ANALYSES

INTRODUCTION

This guideline outlines the minimum suggested quality control (QC) activities for the WMP Benchmark Soil analyses. In cases where labs have been doing more in the way of QC or the WMP Quality Assurance (QA) Plan specifies additional QC procedures, the more stringent guidelines should be used.

These guidelines are set up on a "run" basis. Run is defined here as one day or one continuous set of analyses for a lab.

The purpose of the QC activities is to document data accuracy, precision and comparability. Accuracy is assured by proper calibration and is assessed by analyzing a sample with previously determined results (the WMP ME B reference Soil [WMP-B soil]). Labs are being provided with the expected results for the internal standard.

Precision is assured by keeping instruments calibrated and by uniform procedures. Precision is documented by analyzing routine samples in duplicate and evaluating the standard deviation or percent RSD. The guidelines for the precision goals were developed using Table 10 of the Integrated QA Plan and various appendices of the WMP Quality Assurance Plan and goals for the Direct/Delayed Response Project (DDRP). The data quality objectives (DQOs) are summarized in Table 4 of this appendix. Comparability among laboratories will be assessed by evaluating the results of the WMP-B soil.

Each analytical run should have a unique number or code to identify it. Results for each run should be accompanied by data for the QC samples with every data value linked to the run code.

TYPES OF QUALITY CONTROL SAMPLES

Quality Control Check Sample (QCCS)

A QCCS is a sample that contains the analyte of interest in the mid-range of concentration for what is expected for the routine samples. QCCS samples can be obtained commercially or prepared from a source that is independent of the calibration standards.

The QCCS is analyzed to verify that the calibration of the instrument is still valid. QCCS samples are analyzed after calibration, every 15 samples and at the end of a run (or more often if specified in the Task QA Plan).

WMP-B Soil

The WMP-B soil sample has an established expected range of values, and is to be analyzed along with routine samples to evaluate accuracy (that is, how close is the result to an expected value). One WMP-B soil sample per run should be sufficient.

Reagent Blanks

These blanks are prepared for methods that require sample preparation. The blanks are composed of all the reagents in the same quantities as required for sample preparation. The blank undergoes the same digestion and extraction procedures as routine samples. The measured value of the blanks should be less than or equal to the detection limit. If not, the source of contamination must be identified and corrected.

Detection-Limit Quality Control Check Sample (DL-QCCS)

The DL-QCCS sample is like the QCCS except that rather than being in the mid-range concentrations it is at the low end. The concentration should be 2-3 times the expected detection limit.

This sample should be analyzed once per run. A calculated detection limit can be determined by multiplying by 3 times the between-run standard deviation of the DL-QCCS samples.

Detection Limits

An 'actual' detection limit should be determined periodically (every 6 months). This is done by analyzing a series of dilutions for an analyte and observing where a response can be detected from instrument noise. This replaces the need for "calibration blanks".

Matrix Spike

Matrix spikes are run at the beginning of a run for analyses where matrix effects might be expected. Spike recovery should be 100 ± 15 percent. If there are persistent matrix effects, the run will be analyzed by the method of standard additions.

$$\% \text{ spike recovery} = \frac{\text{value of sample plus spike} - \text{value of unspiked sample}}{\text{value of spike added}} (100)$$

Duplicate Sample Analysis

For each analysis a routine sample should be analyzed in duplicate. For data values below the "crossover" in Table 4, the standard deviation of the pair should be less than or equal to the "lower limit" DQO. Pairs with data values above the crossover point should have a percent RSD less than or equal to the "upper limit" DQO.

The point at which values cross from lower limit to upper limit is calculated by dividing the standard deviation at lower limit by the upper limit RSD (not % RSD).

Ion Chromatography Resolution Test

The resolution test should be run once per run. The test consists of a standard that contains approximately 1 mg/L each of SO_4^{2-} , PO_4^{3-} , and NO_3^- . Resolution should exceed 60 percent for each analyte.

SUMMARY OF GENERAL QUALITY CONTROL

Calibrate instrument daily.

IC resolution check daily where appropriate.

QCCS before routine samples, every 15 and after last routine each run.

WMP-B soil 1 per run.

Reagent blanks (at least one per run).

DL-QCCS 1 per run.

Duplicate analysis of one routine sample, once per run.

Matrix spike(s) each run where appropriate (at least one).

TABLE 4. WMP LABORATORY SOIL DATA QUALITY OBJECTIVES

Parameter	Units	Lower Limit (std)	Upper Limit	Crossover* (%RSD)
Total Nitrogen	g/Kg	0.15 **	10	1.5
Total Carbon	g/Kg	0.5	10	5.0
Total Sulfur	mg/Kg	0.002 **	10	0.02
pH in water	-log(H ⁺)	0.15	same as lower	-
pH in .002M CaCl ₂	-log(H ⁺)	0.15		
CEC NH ₄ Cl	meq/100g	0.25	10	2.5
In NH ₄ Cl				
Ca, Mg, Na, K	meq/100g	0.02	10	0.2
Al	meq/100g	0.20	15	1.3
In .002M CaCl ₂ (from DDRP Mid-Appalachian goals)				
Ca	meq/100g	0.05	5	1.0
Mg	meq/100g	0.005	10	0.05
K	meq/100g	0.005	10	0.05
Na	meq/100g	0.005	10	0.05
Fe	meq/100g	0.01	15	0.07
Al	meq/100g	0.05	15	0.33
Exch Acidity (BaCl ₂ -TEA recommended)	meq/100g	1.0	15	6.7
SO ₄ in H ₂ O, PO ₄	mg S/Kg	1.5 **	10	15
Sulfate isotherms	mg S/L	0.1	5	0.5
Particle Size Analysis			DDRP DQOs	
Sand	wt. %	10%	same	3 STD
Silt	wt. %	10%	same	3 STD
Clay	wt. %	10%	same	2 STD

Incubation for N mineralization QA Plan Appendix N: *Analytical error 1%* *Sampling error 15%*

For analyses not listed, consult the WMP QA Plan

STD - standard deviation

RSD - relative standard deviation

* lower limit DQOs apply below these values

** Lower limit DQO were as % in original WMP QA Plan

Appendix B

QUALITY ASSURANCE FOR WET AND
DRY DEPOSITION MONITORING
WATERSHED MANIPULATION PROJECT,
MAINE

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ABSTRACT

The Environmental Protection Agency (EPA) Environmental Research Laboratory - Corvallis (ERL-C) initiated the Watershed Manipulation Project (WMP) as part of the EPA Aquatic Effects Research Program. The WMP is performing a research project at the Bear Brook watershed located in Hancock County in southeastern Maine (BBWM). The purpose of the WMP is to assess the chronic and episodic effects of altered acidic deposition on a regionally representative watershed and stream and to use this information to improve prediction and assessment procedures. This Quality Assurance (QA) plan is for wet and dry deposition monitoring at the BBWM and is one of several documents that relate specifically to the WMP. The QA/QC procedures in this document for wet and dry deposition monitoring are based, in large part, on procedures developed for the National Acid Deposition Program (NADP) and the National Dry Deposition Network (NDDN), respectively.

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1 INTRODUCTION

The Environmental Protection Agency (EPA) Environmental Research Laboratory - Corvallis (ERL-C) initiated the Watershed Manipulation Project (WMP) as part of the EPA Aquatic Effects Research Program. The WMP is performing a research project in a small watershed (Bear Brook Watershed in Maine (BBWM)) located in Hancock County in southeastern Maine. The purpose of the WMP is to assess the chronic and episodic effects of altered acidic deposition on a regionally representative watershed and stream and to use this information to improve prediction and assessment procedures.

The purpose of deposition monitoring in the WMP is to provide an estimate of time varying inputs to the site. Deposition is an integral component of the input/output budgets that will be calculated during the project.

This Quality Assurance (QA) plan for wet and dry deposition monitoring is one of several documents that relate specifically to the WMP in Maine (Erickson et al. 1990, Thornton and Wigington 1990, and the WMP QA Implementation Plan, FY87-89). This QA plan is mandated by the EPA. QA and quality control (QC) in deposition monitoring for the WMP applies, in general, to field, laboratory, and data management activities. System audits, training, QC samples, QA samples, preventative maintenance, documentation, validation and verification procedures are the various components of the QA system that contribute to a data base of known quality.

Both the wet and dry components of total deposition will be measured during the WMP. Wet deposition includes precipitation in all forms (e.g., a mixture of dissolved particles, gases and undissolved particles in water) (Bigelow 1988). Dry deposition is composed of all other material that is scattered by wind action and deposited at the site.

2 WET DEPOSITION QUALITY ASSURANCE/QUALITY CONTROL

The primary wet deposition monitoring effort in the United States has been by the National Acid Deposition Program in combination with the National Trends Network (NADP/NTN). A goal of the WMP wet deposition monitoring effort is to produce data as comparable as possible to data produced in the NADP network. Because of this, the WMP wet deposition monitoring effort follows portions of NADP's QA/QC protocols (Bigelow 1988, 1984; NADP 1984) including those for siting requirements, field operations, calibration activities, maintenance activities, and documentation. WMP wet deposition data quality objectives (DQO's) for these protocols are similar to those of the NADP (Bigelow 1986).

Other WMP QA/QC protocols that are applicable to deposition monitoring including analyses, reporting, verification, validation, data management, and laboratory corrective actions, are discussed in other sections of the Watershed Manipulation Project (WMP) Implementation QA Plan FY87-89.

WET DEPOSITION MONITORING GOALS

Analytical, parameter specific DQO's (e.g., precision and accuracy) for wet deposition are given in Section 3 of the WMP QA Implementation Plan FY87-89. Goals for the wet deposition sampling effort at BBWM should follow the following NADP protocols as closely as possible:

- Valid sample criteria for precipitation chemistry (NADP 1987) which should be met for the WMP monitoring stations:
 - The sampling interval is 6-8 days;
 - There is a rain gage depth or sample volume reported for the sample;
 - Data are for wet-only deposition samples;
 - Samples are not contaminated.
- For evaluation of data completeness, the following also are considered valid samples:
 - All samples from sampling periods during which it was confirmed that no precipitation occurred are considered valid; and

- Trace samples are considered valid if the rain gage reading is zero or negligible (<0.01 in).

Any deviations from the above should be noted by the site, and made available in data reports.

SITING REQUIREMENTS

Wet deposition will be collected at three sites on Lead Mountain (Figure 1). Two wet deposition monitoring sites (summit and camp stations) were installed during the 1987 field season. The site located at the east weir was installed during the 1988 field season. All NADP instrumentation requirements (Bigelow 1984) were followed at each of the three sites. NADP site installation criteria (Bigelow 1984, 1988) were followed with three exceptions:

- The ground slope changes more than 15% within 30 m in almost all directions from each gage and collector,
- The distance between each collector and rain gage is approximately 3 meters, which is less than the recommended 5 meters,
- The top heights of a collector and rain gage should be within one foot or less of each other. The top heights of the collector and rain gage at the summit and camp stations are within two feet of each other.

FIELD OPERATIONS

The site operator for the three WMP monitoring installations is J. Scofield, University of Maine, Orono. The site supervisor is Dr. S. Norton, University of Maine, Orono.

The site operator of the WMP wet deposition stations is responsible for:

- All weekly sample collection activities and transport of samples to Orono immediately after sampling;
- Completion of all field measurements;
- Completion of the weekly sampling documentation;

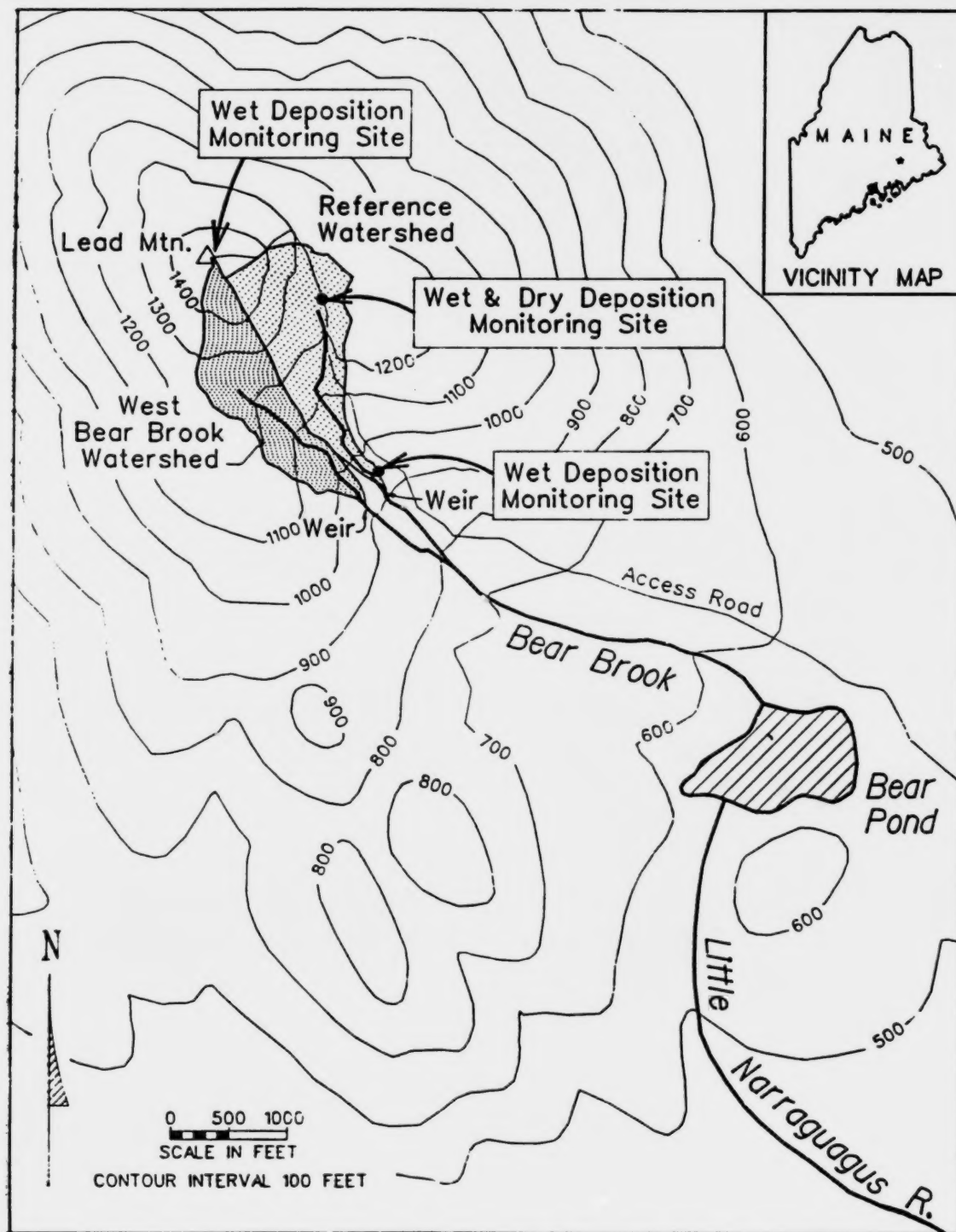


Figure 1. Wet and dry deposition monitoring sites for the Watershed Manipulation Project.
B-4

- Required maintenance to all instruments at the site; and
- Instrument calibrations at the site.

Sampling/Measurement

Wet deposition will be monitored at three field sites (Figure 1). Sample collection protocols were derived from the procedures outlined in the NADP/NTN Site Operation Manual (Bigelow 1988). Specific sample collection and handling protocols for the Lead Mountain sites were prepared by the site operator (J. Scofield) and are summarized in this section.

Each site consists of an Aerochem Metrics wet/dry collector and a Belfort 12 inch rain gage. Each Tuesday, the Aerochem collection bucket and the rain gage chart are changed at each site. In addition to the wet-dry collector and the rain gage, three other types of deposition collection techniques are utilized at each site if snow has fallen during the previous week. These are "large pail" precipitation samples, snow core samples, and snow tube samples. The first two are used as QC checks on precipitation volume and chemistry if necessary and the latter is used to determine the water content of the present snow pack. The large pail sample is only collected and processed in the unlikely event that snow depth exceeds the Aerochem bucket capacity, as a malfunction occurs.

Sample Container Preparation

All containers used for wet deposition sample collections, except lids, are acid washed prior to their use in the field. Acid washing involves immersing the containers, and other plasticware, except lids, in an acid bath of 10% HCl. The wet-dry bucket is rinsed with a solution of 10% HCl. The lids are cleaned by rinsing three times with deionized water; acid rinsing would cause corrosion of the rubber rim on the lids. The containers are rinsed a total of 7 times. First, they are rinsed two times with warm tap water, then three times with reverse osmosis water, and finally, two times with deionized water.

Approximately 500 ml of deionized water is placed in the wet-dry bucket, except when field temperatures are below freezing and the lid secured with a velcro strap. All other plastic ware used during the collection are placed in plastic bags.

Container and Sample Transport

All containers and instruments are transported to Lead Mountain via automobile or truck. Upon arrival, the smaller containers and instruments are placed in an internal frame pack for ease of transport to the sample sites. The wet-dry buckets are hand-carried up the mountain to the sites.

Samples are also transported from Lead Mountain back to the laboratory via automobile or truck. Nalgene™ bottles and "large pail" snow samples are carried down the mountain in an internal frame pack. The wet-dry buckets are hand-carried down the mountain. If the wet-dry buckets contain only water, the water is transferred to Nalgene™ bottles at each of the monitoring sites. Sample preservation is performed upon arrival at the laboratory.

Field Protocols

Sample Collection -

Upon arriving at the sample site, the Velcro™ strap and lid are removed from the "new" bucket and the spring-loaded clasp that secures the collection bucket to the Aerochem instrument is disengaged from the handle of the "old" wet bucket. Next the sensing unit that controls the position of the precipitation lid on the wet/dry collector is moistened so that the lid moves from the wet bucket to the dry bucket, allowing the operator access to the wet bucket. The wet bucket is then removed, labeled (with the date and time of collection, operators initials and the site ID), and the new bucket placed in the sampler. The spring loaded clasp is engaged to secure the new bucket to the stand.

If the bucket just removed contains snow or ice, then the plastic lid is placed on the bucket and secured with the velcro strap and the bucket is transported to the laboratory.

The precipitation is transferred from the bucket to 1000 ml Nalgene bottles, if the bucket contains only rain water. This is accomplished by first vigorously shaking the Nalgene bottles and using the deionized water to rinse a funnel. The contents of the bucket are poured into the Nalgene bottles. Then lids are secured on the bottles and the bottles are labeled and are transported to the laboratory.

Rain Gage Charts -

Rain gage charts for the upcoming week are prepared by marking the date, time, operators initials, sample site, and any other pertinent comments in the space provided on the chart. At the site, a tick mark is made on the current chart indicating the time and date that the chart was removed. The pen is pulled off the chart so that the operator has easy access to the drum itself. The drum, which holds the chart, is then removed and the clock is wound and inspected to insure that it is working properly. The old chart is removed from the drum and the new one put into place. The drum is then placed back on the instrument and secured with the bolt provided. The pen is then moved so that it is in contact with the chart and the operator makes a tick mark with the pen to indicate the time and date the new chart was put into operation and also the level of water in the instrument at that time. The previous week's chart is brought back to the laboratory where information regarding daily precipitation is recorded. Afterwards, the chart is placed in a notebook for future reference.

Large Pail Collector -

The large pail collector is a 20 gallon, plastic trash can secured to a wood post, which is attached to the side of the platform on which the wet-dry collector sits. Its purpose is to collect weekly snow events to allow an estimate of the snowfall for weeks that exceed the capacity of the wet-dry bucket.

Large pail precipitation samples are collected by first untying a rope that secures the top 10 inches of a plastic bag to the outside of the container. The top of the bag is then gathered together and twisted before removing the bag and contents from the pail. After removing the bag, the upper part of the bag is secured and labeled with the date and time of collection, operators initials and site ID. The entire bag is

then placed into a second bag, which is also secured. The package is then placed in an internal frame pack for transport to the laboratory.

Next, a new sample collection bag is put into place. This is done by placing the bottom of the bag into the collector, and while lowering the bag, pulling it apart by its sides so that it fills the bucket as completely as possible. The bags are approximately 10 inches deeper than the garbage can. This excess is folded over the top of the bucket and secured. The inside of the bag is not touched throughout the process.

Snow Cores -

If precipitation falls as measurable snow during any previous week, snow core samples may be collected. The snow core samples are collected with a three foot length of 1.5 inch diameter PVC pipe. Cores are collected by pushing the PVC pipe vertically through the snow pack until it touches a 4 ft by 4 ft sheet of plywood placed at the sample site that is cleaned on each sample date. A stainless steel spatula is inserted between the plywood and the bottom of the core and the core is transferred to the first of two, 2-liter Nalgene bottles. This process is continued until the second 2-liter bottle is filled with snow. The lids are secured on the bottles and they are appropriately labeled. The depth of the snowpack at each core is measured and recorded, as well as the number of cores necessary to fill the bottle when each core is collected. The snow core samples are used as a quality check of the wet-dry bucket chemistry.

Snow Tube Samples -

Snow tube samples are collected to determine the water content of the snow pack. These are collected using a Snow Sample Tube and weighing scale purchased from LIFE-LINK International, Inc. of Jackson Hole, Wyoming.

The weighing scale is zeroed before starting with the collection. The samples are collected by pushing the end of the snow tube vertically through the snow pack until contact is made with the soil surface. The spatula is used so that the tube can be inverted without losing any snow. The hook on the scale is then attached to the tube and millimeters of water contained within the tube are read directly off of

the scale. The depth of snow at the sample site and the millimeters of water are recorded in a field notebook. This procedure is repeated five times at each sample location. Each week the sample location varies within a cordoned off area near each met station.

Sampling Handling After Collection

Sample volumes are determined before any chemical analyses are performed at the laboratory. The buckets are weighed and the sample volume is the difference in weight between the full buckets and the empty bucket weights of the bottles. After the weights are determined, the sample is transferred to 500 ml bottles (in the lab), and stored at 4°C until the laboratory is ready to begin analyses. Samples are analyzed for all parameters shown in Table 1.

Snow core samples and Aerochem samples are allowed to melt in their containers in the case of snow core samples, large pail precipitation samples, and Aerochem samples that contain snow and/or ice. The snow core samples are then weighed to determine volume of precipitation. Aerochem samples are transferred to 500 ml Nalgene bottles, weighed and stored as described above. The large pail precipitation samples are handled in one of two ways depending on the volume of snow collected during the week. If the volume is small enough such that it will fit into an empty wet-dry bucket, the plastic bag containing the snow sample is emptied into a wet-dry bucket for melting. Volume of sample is then determined as with Aerochem samples. If the volume of snow is such that it would not fit into an empty wet-dry bucket, the snow is allowed to melt inside the plastic bag. After the snow has completely melted, the total volume in the bag is transferred to 500 ml Nalgene bottles. Volumes are then determined as described above.

Watershed Manipulation Project Sampling QC Considerations

The following QC considerations apply to the sample collection and field measurement portion of the WMP deposition monitoring effort:

- Accuracy of sample weights should be ± 1 g;

Table 1. Precipitation and snow chemistry parameters and analytical methods.

Maine Site Laboratory Analyses	
<u>Parameters</u>	<u>Analytical Method Information</u>
Acid Neutralizing Capacity (ANC)	Gran Titration, Driscoll & Bisogni (1983)
Anions: SO ₄ , NO ₃ , Cl, F	IC ¹ , Tabatabai & Dick (1983)
Cations: Ca, Mg, Na, K	AAS ² , Hillman et al. (1986)
Ammonium (NH ₄)	Autoanalyzer, Hillman et al. (1986)
Aluminum, total	Filtered, acidified
pH, aerated	Electrode, Hillman et al. (1986)
pH, unequilibrated	Electrode, Hillman et al. (1986)
Specific Conductance	Wheatstone Bridge, Hillman et al. (1986)
Apparent Color	Optical comparator on unfiltered sample

¹Ion Chromatograph

²Atomic Absorption Spectrophotometer; Ca and Mg with N₂O - acetylene flame, Na and K with air-acetylene flame.

- Wet/dry collector catch efficiency should be 90-110% efficient (this means the wet/dry collector in relation to the Belfort rain gage). Summer efficiency is usually higher (about 100%) than the winter efficiency (about 80-90%) for this region); and
- Rain gage accuracy should be ± 0.05 in (sand bottle tests are used to evaluate accuracy; recommended once per year).

The following routine QC Field Samples will be utilized at the given frequencies:

- Replicate samples - replicated samples are prepared each collection date if volume permits and are used for precision estimates;
- Field blanks - one field blank per month is prepared to monitor for sample contamination; and
- External audit material - audit samples will be distributed on a quarterly basis at the laboratory level, which allow evaluation of analytical accuracy.

In addition, site visits will be conducted by ERL-Corvallis personnel to monitor sampling collection techniques, calibration and preventive maintenance activities.

Watershed Manipulation Project Sampling QA Considerations

QA considerations associated with the WMP deposition monitoring effort include:

- Operator training for proper protocols, which will be carried out previous to the initial sample collection trip;
- Evaluation of the data for precision, accuracy, comparability, and completeness according to protocols presented in this document and the WMP QA Implementation Plan, FY87-89; and
- Field data sheets evaluation. These evaluations will take place on the day following sample collection and include reviewing all categories that are documented (e.g., if precipitation is greater than 0.5 in, collector and rain gage should be within 15%).

CALIBRATION ACTIVITIES

Calibration activities presented in the NADP/NTN Site Operation Manual (Bigelow 1988) are followed.

Instruments that require calibration at the WMP site include:

- The collector;
- The rain gage twice per year; and
- Temperature thermistors.

MAINTENANCE ACTIVITIES

Weekly and periodic maintenance protocols in NADP (Bigelow 1988) are followed at each of the monitoring stations. These include:

- Weekly maintenance:
Aerochem - precipitation sensor, event recorder showing sampler open and closed;
Event recorder - as above.
- Periodic maintenance:
Aerochem - wash rain sensor grid, check for short (8 weeks) - wet/dry buckets removed, underside of Aerochem lid cleaned with DI water or tissue;
Rain gage - winterizing and biannual calibration.

Quality Control Considerations for Maintenance

The following QC activities are performed at the WMP wet deposition monitoring sites:

- Instrument calibration - NADP protocols (Bigelow 1982);
- Lid seal effectiveness - checked weekly;
- Sensor checks - checked weekly; and
- Weighing calibration or sand bottle testing - checked quarterly.

DOCUMENTATION (SEE ON-SITE MANUAL FOR PROTOCOLS)

A field observation report developed after the NADP form (Bigelow 1988, Field Observer Report Form) is filled out during sample collection. These reports are reviewed on a weekly basis and filed for review by auditors.

LABORATORY QUALITY ASSURANCE/QUALITY CONTROL

Laboratory QA/QC protocols for wet deposition analyses and DBM are covered in Sections 6 of the WMP QA Implementation Plan, FY87-89.

DATA MANAGEMENT QUALITY ASSURANCE/QUALITY CONTROL

Data management associated with wet deposition monitoring results is discussed in Section 6 of the WMP QA Implementation Plan, FY87-89.

SYSTEM AND PERFORMANCE AUDITS OF FIELD OPERATIONS

Personnel from ERL-Corvallis and representatives of the Site Supervisor conduct on-site audits at the Lead Mountain sites every two years. These audits evaluate equipment as well as on-site activities performed by the Project staff. The following equipment is evaluated:

- Aerochem Metrics Wet/Dry collector (sand bottle and turnover performance testing - (Bigelow 1986);
- Rain gage;

Operator audits include a critical review of the Field Observer Report Forms that accompany each weekly deposition sample. This form includes: daily precipitation records, field sample bucket weights, and QA checks performed by the site operator each time a sample is collected. The evaluation follows NADP guidelines for evaluation of their field observer report forms that is given in Bigelow (1986).

CORRECTIVE ACTIONS

Necessary corrective actions in the field are identified by the site operator, implemented and documented. Corrective actions associated with laboratory operations are discussed in Section 6 of the WMP QA Implementation Plan, FY87-89.

3 DRY DEPOSITION MONITORING

A National Dry Deposition Monitoring Network (NDDN) is in its early stages in the United States. EPA, through a contractor, Environmental Science and Engineering (ESE), has recently developed standard site instrumentation, sampling, preservation, and QA/QC protocols for this dry deposition monitoring Project. A dry deposition station is planned for the BBWM site. The WMP dry deposition monitoring effort will follow the protocols presented in the National Dry Deposition Network Project Quality Assurance Plan (ESE, 1987a).

Protocols relevant to the WMP follow Standard Operating Procedures for the following major disciplines:

- Site installation and initiation;
- Field operations; and
- Site operator's training.

QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The QA objectives for dry deposition measurement data are expressed in terms of precision, accuracy, completeness, representativeness, and comparability. The QA objectives that apply in the WMP for each of these categories are given in ESE (1987a). Relevant QA objectives to the University of Maine personnel include:

- Sample handling protocols;
- Sample integrity requirements; and
- Sample custody.

SITING REQUIREMENTS

As with the WMP Wet Deposition stations, all of the general site selection criteria for the NDDN might not apply to the WMP Dry Deposition station because of site-specific WMP objectives versus the objectives of the NDDN.

FIELD OPERATIONS

The University of Maine site operator and sampling crews have responsibility for dry deposition sample collection (field operation), transport of tapes to EPA at Research Triangle Park, NC (RTP), transport of filter packs to the ESE laboratory in Gainesville, Florida, and instrument maintenance.

Sampling/Measurement

Field QC protocols are presented in ESE (1987a) and include protocols for:

- Air Filter Packs;
- Windspeed and direction;
- Relative humidity;
- Solar radiation;
- Precipitation (tipping bucket rain gage); and
- Ambient temperature (cross checked with University of Maine sensors).

The following QC considerations for sampling/measurements apply to the WMP dry deposition monitoring effort.

- Backup Data Acquisition System (DAS) installed at the site;
- Field blanks (filter pack); and
- QC charts (analytical responsibility of ESE through EPA-RTP).

Sample Transportation

Sample transportation is ultimately the responsibility of the site supervisor although the site operator carries out the actual shipment activities. Two routine sample shipment activities are associated with the dry deposition monitoring effort of the WMP:

- Filter packs will be shipped to ESE in Gainesville, Florida for analysis; and
- DAS tapes will be shipped to RTP for downloading and analysis.

All shipments are sent by overnight carrier.

Calibration Procedures

Table 6-1 in ESE (1987a) will be followed for analytical procedures. Field calibration procedures. Calibration checks at the site will be performed by University of Maine personnel.

Preventive Maintenance

Preventive maintenance procedures are discussed in ESE (1987a). These include maintenance procedures for both field and analytical instruments. Field maintenance will be performed by University of Maine personnel.

ANALYTICAL PROCEDURES

Table 2 presents all analytical methods to be utilized for dry deposition sample analyses (from ESE 1987a). All dry deposition analyses will be performed by ESE under subcontract to EPA-RTP. Internal analytical QC procedures also are presented in ESE (1987a).

DATA MANAGEMENT (REDUCTION, VALIDATION, REPORTING)

Data acquisition and storage, field data forms, labeling will follow EPA-RTP NDDN protocols. Data validation will also follow NDDN protocols and will be performed by EPA-RTP. Validated data will be transmitted from EPA-RTP to ERL-Corvallis on a quarterly frequency.

PERFORMANCE AND SYSTEMS AUDITS

The WMP site will participate in an annual field systems audit program managed and operated by NDDN personnel. All of the topics evaluated during these audits might not apply to the WMP site (e.g., siting criteria to meet regional objectives). Field performance will be the focus of these audits.

Laboratory performance audits will be performed by NDDN personnel in connection with routine NDDN analytical reviews of their analytical facilities. Since the data management system for the dry deposition data collected on Lead Mountain will be the same as that utilized for the NDDN, all auditing procedures will be the same as for the National Network.

CORRECTIVE ACTIONS

All corrective actions regarding the monitoring station on Lead Mountain and the triggering mechanisms for requiring them are discussed in ESE (1987a).

Table 2. Summary of Laboratory Analyses Planned for NADP (from ESE 1987a).

Reporting Limit Parameter	Analytical Technique*	Matrix
Calcium (Ca^{+2})	Flame Atomic Absorption	Water
Magnesium (Mg^{+2})	Flame Atomic Absorption	Water
Sodium (Na^{+})	Flame Emission	Water
Potassium (K^{+})	Flame Emission	Water
Ammonium (NH_4^{+}N)	Automated Colorimetry	Water
Nitrite (NO_2N)	Ion Chromatography	Water
Nitrate (NO_3N)	Ion Chromatography	Water, Filter Extract
Sulfate (SO_4^{2-})	Ion Chromatography	Water, Filter Extract

*Refer to the Laboratory Operations Manual for analytical procedure.

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APPENDIX C

QUALITY ASSURANCE PLAN FOR INDIVIDUAL TASK COOPERATORS

NOTE: References cited in this Appendix are included in Section 6.

APPENDIX C-1

A REGIONAL EVALUATION OF PROCESSES REGULATING THE TRANSFER OF ALUMINUM BASIC CATION PRIOR TO AND FOLLOWING STRONG ACID APPLICATION

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TASK DESCRIPTION

Research Objective: To evaluate regional differences in processes regulating the transfer of Al and basic cations prior to and following strong acid application.

In this research, laboratory, field plot and catchment scale manipulations, will be used to test research hypotheses concerning the release of basic and acidic cations from soils to surface waters. All field studies will be performed at the U.S. EPA Watershed Manipulation Project (WMP) site in Maine. Laboratory studies will be conducted using soils, soil solutions and stream water from this site. The advantage of conducting studies of cation release from forested watersheds through the WMP is that process-level laboratory and field plot experiments can be integrated with studies on hydrology and other element cycles (e.g., S, N and C) being conducted by other cooperating WMP researchers. These projects will be integrated with whole-watershed manipulations conducted by site researchers, thus fostering a mechanistic understanding of the chemical and ecological interactions producing soil and surface water acidification.

In this study we propose to test a series of research hypotheses by:

1. Conducting batch laboratory studies using soils collected from the WMP site at Maine to evaluate cation exchange relationships in order to establish cation selectivity coefficients for WMP models and to evaluate the utility of this approach as compared to alternative formulations of cation exchange. (SUNY Plattsburgh)
2. Conduct batch laboratory studies using soil collected from the WMP site at Maine to evaluate specific cation selectivity between cation-pairs. (SUNY Plattsburgh)
3. Conduct titrametric laboratory studies using Oa horizon leachate collected from the WMP site at Maine to evaluate Al-DIC interactions in organic carbon coagulation/retention and the stability of alumino-organic complexes. (Syracuse University, SUNY Plattsburgh)
4. Conduct batch laboratory studies using soil collected from the WMP site at Maine to evaluate mineral dissolution/cation exchange reactions important in the regulation of Al concentrations. (SUNY Plattsburgh)
5. Conduct laboratory column studies using soil collected from the WMP site at Maine to evaluate the effects of increased mobile anion loading on Al and basic cation release. (Syracuse University with SUNY ESF)
6. Conduct laboratory column studies using soil collected from the WMP site at Maine to investigate interactions between primary and secondary mineral dissolution and cation exchange. (Syracuse University with University of Iowa and University of Wyoming)
7. Conduct field plot experiments at the WMP site in Maine to investigate the effects of increased acid loading and anion mobility on Al chemistry and release of basic cations from soils. (Syracuse University)
8. Conduct catchment level experiments in cooperation with site leaders at the WMP site in Maine to investigate the effects of increased acid loading on surface water acidification in general and specifically on Al chemistry and base cation release. (Syracuse University)

Laboratory investigations, which generally use well mixed or composited soil or solution aliquots collected from the WMP site at Maine, will routinely be performed at least in duplicate for all treatment combinations.

Field plot studies involving dosing of acids to forest soils will be conducted. These studies will utilize a randomized complete block or similar design compatible with the research site to account for large scale spatial variability.

Catchment scale manipulations will utilize the paired watershed approach (Likens, *et al.* 1977), in which an untreated control watershed is paired with a treatment watershed. Because of the expense involved in whole watershed treatment and monitoring, replication of these types of experiments has generally not been possible. Consequently, a pretreatment calibration period is used to establish statistical relationships between variability in the reference and treatment watersheds. Following treatment, these statistical relationships are periodically re-evaluated to determine if a significant change has occurred. Typically, this involves testing for changes in a linear regression slope and/or intercept using standard parametric techniques. Most of the catchment-scale monitoring will be performed by the site leaders.

In both field plot and whole-catchment studies, researchers at Syracuse University will analyze soil samples for cation exchange capacity (CEC), exchangeable cations (Ca, Mg, Na, K, Al and Fe), free (non-silicate bound) Al and Fe fractions and solutions (throughfall, soil solutions, groundwater, streamwater) for aqueous Al fractions.

ORGANIZATION AND RESPONSIBILITIES

Researchers at Syracuse University will conduct analysis of free (non-silicate bound) Al and Fe fractions and aqueous Al fractions on the Maine WMP soils and solutions as part of the field plot and whole-watershed studies. Researchers at SUNY Plattsburgh will measure CEC and exchangeable cations from the Maine WMP soils as part of the field plot and whole-watershed studies. Batch laboratory experiments will be conducted at SUNY Plattsburgh to evaluate selectivity coefficients and Al solubility for Direct/Delayed Response Models, as well as the pH-dependence of these processes. Laboratory titration experiments to characterize alumino-organic interactions will be conducted by researchers at Syracuse University and SUNY Plattsburgh using dissolved organic carbon (DOC) from organic horizon leachate collected from the WMP site at Maine. Laboratory column experiments to evaluate the response of cations through exchange and dissolution processes to different acid loadings will be conducted by researchers at Syracuse University.

Dr. C.T. Driscoll of Syracuse University and Dr. R.D. Fuller of SUNY- Plattsburgh, Principal Investigators of this project, will have overall responsibility for project measurements, sample custody and data reporting. Dr. D.C. McAvoy of Syracuse University will also supervise sample collection, analytical measurements, sample transfer and handling, as well as data quality and transfer. Their quality assurance responsibilities include:

- Monitoring daily QA/QC activities,
- Reviewing laboratory notebooks, instrument performance logs, and QA/QC data on a regular basis,
- Determining that performance audits, triplicate analyses and other QA/QC activities are performed,
- Examining data summaries and calculations,

- Assisting in trouble-shooting problems,
- Preparing quarterly QA summaries and reports,
- Checking that all project personnel are competent to perform analyses, and
- Ensuring that all QA/QC operations are followed.

A field technician, partially supported by the AI task group, will have the responsibility to:

- Maintain instrumentation at the WMP field plot and watershed site in Maine,
- Assist WMP site personnel in sample collection including field blanks and replicate samples,
- Process aqueous samples for the fractionation of AI,
- Ship AI extracts and soil samples for analysis to Syracuse University and SUNY Plattsburgh,
- Maintain appropriate notebooks of field activities and sample log,
- Observe and record events that may effect field data, and
- Report problems to the principal investigators.

Laboratory chemists, technicians, and graduate research assistants have the responsibility to:

- Understand their role in the project and laboratory,
- Maintain appropriate notebooks, instrument logs, and QA/QC records,
- Observe and record events that may affect experimental data,
- Report any problems or concerns to the principal investigators, and
- Perform routine maintenance on instrumentation as required.

Regular meetings of the project personnel will be held to discuss experimental progress, analytical problems or concerns, or any other problems within the project.

QUALITY ASSURANCE OBJECTIVES

An assessment of field and laboratory data requires an understanding of the precision and accuracy associated with analytical determinations. A summary of expected data quality objectives is presented in Table C-1-1.

SAMPLE PROTOCOLS

Soil samples will be collected and sieved in the field (12 mm), put into plastic bags, and labelled with date, site, pedon and horizon identifiers by the site group. A field technician partially supported by the AI task group will assist in sample collection, sample processing and sample custody at the field site.

Field solution samples (throughfall, soil solution, stream water, snowmelt) for Al fractions will be collected, labelled, and extracted by the site group in accordance to their sampling protocol. These samples will then be shipped to Syracuse University for analysis.

Laboratory - All water samples from laboratory experiments will be collected in prelabelled, HCL-washed (1.0 N) polyethylene containers which are soaked (>12 hours) and rinsed (>5 times) with deionized water. Sample containers will be rinsed (three times if sample volume is adequate) with sample solution prior to collection. Soil samples, from field and column studies, will be air dried and sieved (2 mm) prior to analysis. Subsamples will be dried at 110°C for oven-dry weight determinations.

SAMPLE CUSTODY

The concentration of certain water parameters in field and laboratory-derived solutions will change after sample collection. This problem is particularly pronounced in low ionic strength waters that are poorly buffered. Therefore proper procedures for storage and handling are critical for an accurate chemistry monitoring program. Parameters that are susceptible to change will be analyzed (e.g., pH, DIC, DOC, NH_4^+ , NO_3^-) or processed for analysis (Al fractions) shortly after collection. Water samples collected in the field will be shipped on ice and both water and soil samples will be transported to Syracuse University by a parcel carrier. Samples will then be stored at 4°C in the Environmental Engineering Laboratory at Syracuse University until they are analyzed. Syracuse University field and laboratory technicians will monitor sample custody and transfer. Any soils needed for analysis by Plattsburgh will then be shipped from Syracuse.

ANALYTICAL PROCEDURES

Water and soil chemistry constituents measured in this study are determined using standard methods in water and soil analysis as presented in Tables C-1-2 and C-1-3, respectively. Methods are generally similar to those used in the Direct/Delayed Response Program, which are described in Blume et al. (1986) and Cappel et al. (1986). The procedure for determining monomeric Al fractions is described in Barnes (1975) and Driscoll (1984).

CALIBRATION PROCEDURES

Atomic Absorption Spectrophotometer

This instrument is calibrated with 4-7 standards at the start of each run. QC standard checks are run every 10-20 samples and standards rechecked at the end of each run. If the standard checks are in error by more than 5% the instrument is recalibrated and the samples up to this point are rerun. Standards are prepared with ACS reagent grade chemicals or from atomic absorption reference standards.

Ion Chromatography

Calibration procedure same as AAS.

Organic/Inorganic Carbon Analyzer

Calibration procedure same as AAS.

Ion Selective Electrode Meter

Calibration procedure same as AAS.

pH Meter

This instrument is calibrated initially with pH 7.00 and 4.01 NBS certified buffers before each set of measurements. To evaluate electrode performance, a low ionic strength standard (pH 4.7) is analyzed before each run. Calibration is rechecked after 2 hours of continuous use and at the end of the analysis session.

Automatic Titrator

Calibration procedure same as pH meter

PREVENTATIVE MAINTENANCE

Instruments used in the Environmental Engineering Laboratory at Syracuse University and at the Miner Agricultural Research Center associated with SUNY Plattsburgh are maintained in accordance to manufacturer's specifications.

Atomic Absorption Spectrophotometer

Flame mode: Routine maintenance includes cleaning the burner head slot with a razor blade when an uneven flame is noticed. Furthermore, if low absorbance readings are detected on standards, and the burner head slot is clean, the nebulizer and/or sample capillary is checked for obstruction. If aspirating deionized water fails to clean the sample and/or nebulizer capillary, a wire is pushed through the capillaries to remove the obstruction. For deposits that do not yield to either of these measures, the nebulizer is disassembled for cleaning.

Furnace mode: Routine maintenance consists of replacing the graphite contact rings if there is any sign of pitting on the contact surfaces or any excessive sign of wear. Graphite tubes are also replaced every 400-500 samples or when variability of results become high.

Ion Chromatography

Monthly maintenance consists of lubricating the analytical pump motor, cleaning the conductivity detector cell electrodes and checking the cell calibration. Periodically the interior of the Advanced Chromatography Module is checked for leaks or spills.

Carbon Analyzer

Routine maintenance of the carbon analyzer consists of replacing the injection septum every 100 injections or when leakage is obvious, as well as replacing the pump tubes at approximately two week intervals during periods of continuous operation. The tin scrubber tube is repacked when about half of the tin is exhausted. The lithium hydroxide scrubber is checked periodically with a 50 ppm carbonate standard and is repacked if break-through is seen. The cupric oxide packing is inspected on a bi-monthly basis and replaced as needed.

Ion Selective Electrodes and Meters

There is no routine maintenance procedure for the ion selective electrode meters. To insure a long life of the electrodes the fluoride ion selective electrode is stored in air, the single junction reference electrode is stored in deionized water, and pH combination electrode is stored in pH 7 buffer solution between analyses.

INTERNAL QC CHECKS AND CORRECTIVE ACTION

Quality Control Samples

Quality control samples will be prepared from a source independent of the calibration standards for cation (AAS) and anion (IC) analyses. QC samples will be analyzed with each run and if results are not within 5% of expected values, recalibration and standardization of the instrument will be performed. In addition to the internal QC samples, we periodically evaluate blind samples obtained from the U.S. EPA Municipal Environmental Research Laboratory at Cincinnati, Ohio, the USGS Standard Reference Water Sample Program in Denver, Colorado, and the U.S. EPA Long-Term Monitoring Program through Radian Incorporated. This practice will be continued throughout the duration of this study.

Blank Analysis

A calibration blank (0 mg/L) will be run every 10-20 samples. If the calibration blank is not less than twice the detection limit (see Table C-1-1) the instrument will be rezeroed and recalibrated.

Replicate Sample Analysis

Triplicate sampling and triplicate analysis will be made on a minimum of 5% of the laboratory samples to evaluate sampling and analytical precision. In addition, 5% of the field samples will be collected and analyzed in duplicate.

Electroneutrality and Conductivity Balance

The accuracy of analytical determinations will be evaluated by electroneutrality and conductivity balance checks. These analyses are useful for solutions with low DOC levels and will be performed only when major solution cations and anions are measured.

Corrective Action

All analytical data will be screened by the task group's research associate before any of the solution or soil samples are discarded. When problem data are discovered, samples will be rerun. If sufficient sample is not available for rerunning analyses, the suspect data will be rejected from the data set.

PERFORMANCE AND SYSTEM AUDITS

The Environmental Engineering Laboratory at Syracuse has and will continue to participate in external quality assurance evaluations. Samples are also routinely split with other researchers who analyze low ionic strength solutions (e.g., Cornell University, University of Virginia, and Rensselaer Polytechnic Institute). This program is used in all of our on-going research projects and we plan to continue to use it in the field monitoring and laboratory investigations conducted for the Watershed Manipulation Project. Soil and solution samples will also be routinely split between Syracuse University and SUNY Plattsburgh.

The WMP Performance Audit Program will provide blind audit samples from EMSL-LV on a quarterly frequency for the following parameters to both the Syracuse University (Driscoll) and SUNY Plattsburgh (Fuller): anions, base cations, DOC, NH_4 , pH, and Si. In addition, the Syracuse University lab will analyze audit samples on a monthly frequency for total-Al and Al fractions as part of the monthly audit program for the field solutions. Syracuse University will participate in the Forest Response Program (FRP) Soil Sample Exchange Program for the following parameters: Al fractions, Fe fractions, and pH. SUNY Plattsburgh will participate in the FRP soil exchange for the following parameters: CEC, exchangeable bases, and exchangeable acidity. Both Syracuse University and SUNY will participate in the EMSL-LV Soils Exchange Program.

System audits will be conducted in cooperation with EPA at least annually.

DATA REDUCTION, VALIDATION, AND REPORTING

Reduction

Data results will be recorded in laboratory notebooks, dated and signed by the technician performing the analyses. Printouts from the various instruments will be archived in a separate folder. The logged data will then be transferred to files on an IBM PC (LOTUS 123) and checked for transcription errors by crosschecking back to original data forms. A flow chart of this data reduction scheme is presented in Figure C-1-1.

Validation

Data will be checked for outliers by running range queries in the LOTUS 123 data base management system. If values are rejected they will be verified and if possible reanalyzed. When major cations and anions are measured, accuracy of solution values will be analyzed by performing charge balance and specific conductance checks.

Reporting

Data analysis and reporting will be facilitated by a variety of statistical (SAS), data processing (LOTUS 123), word processing (Wordstar), and graphical (Golden Graphics, Energraphics) software packages. When necessary, files will be uploaded to a mainframe computer (IBM 3090) at Syracuse University where additional analysis can be accomplished with the statistical package SAS (Barr *et al.* 1979). Once data generated at Syracuse are verified, they can then be transferred to the Project's overall data base via floppy disc or BITNET.

REPORTING OF QUALITY ASSURANCE

Analytical precision and accuracy checks when collected will be included with quarterly and annual reports to the Project Officer at EPA.

TABLE C-1-1. QUALITY ASSURANCE OBJECTIVES

Parameter	Units	Range	Precision	Accuracy
pH	pH	3 - 7	3%	5%
ANC	$\mu\text{eq/L}$	-50 - 100	20%	30%
Ca	$\mu\text{mol/L}$	2 - 500	5%	20%
Mg	$\mu\text{mol/L}$	2 - 65	5%	10%
Na	$\mu\text{mol/L}$	2 - 90	5%	10%
K	$\mu\text{mol/L}$	2 - 55	5%	20%
ammonium	$\mu\text{mol/L}$	2 - 15	35%	20%
total Al	$\mu\text{mol/L}$	1 - 40	15%	20%
monomeric Al	$\mu\text{mol/L}$	1 - 40	20%	20%
non-labile Al	$\mu\text{mol/L}$	1 - 40	15%	20%
sulfate	$\mu\text{mol/L}$	3 - 75	10%	10%
nitrate	$\mu\text{mol/L}$	1 - 70	10%	10%
total F	$\mu\text{mol/L}$	1 - 15	5%	10%
Cl	$\mu\text{mol/L}$	1 - 15	10%	35%
DOC	$\mu\text{mol/L}$	5 - 85	15%	35%
DIC	$\mu\text{mol/L}$	2 - 85	5%	20%

TABLE C-1-2. METHODS FOR ANALYSIS OF SOLUTION SAMPLES PRODUCED IN FIELD AND LABORATORY EXPERIMENTS OF THE WMP.

Component	Method	Reference
$\text{SO}_4^{2-}, \text{NO}_3^-; \text{Cr}$	Ion Chromatography	Small <i>et al.</i> 1975
NH_4^+	Ion Chromatography	Small <i>et al.</i> 1975
$\text{Ca}^{2+}, \text{Mg}^{2+}$ Na^+, K^+	Atomic Absorption Spectrophotometry, Flame Atomization	Slavin 1968
Total Monomeric Al (Al_m)	Hydroquinoline extraction into methyl isobutyl ketone, analysis by AAS with graphite furnace	Barnes 1975
Non-labile (organic) Al (Al_o)	Fractionation by ion exchange column, analysis for Al_m	Driscoll 1984
Labile (inorganic) Al (Al_l)	$\text{Al}_m - \text{Al}_o$	Driscoll 1984
Total F	Ion Selective Electrode, TISAB addition	Orion 1976
Silica complex colorimetry	Autoanalyzer; heteropoly blue	Standard Methods 1985
Dissolved Organic Carbon	Filtration, per sulfate oxidation, detection by infrared analysis	Dohrmann 1984

TABLE C-1-3. CHEMICAL METHODS FOR ANALYSIS OF WMP SOILS

<u>Soil pH</u>	1 : 1 soil : DI water ratio for mineral horizons 1 : 5 soil : DI water ratio for all organic horizons 1 : 2 soil : 0.01 M CaCl ₂ for mineral horizons (USDA/SCS 1984)
<u>Cation Exchange Capacity</u>	NaCl replacement procedure for acid soils. Extraction on mechanical syringe extractor. Detection by AAS. (Rhoades 1982)
<u>Exchangeable Bases</u>	Extraction with 1 N NH ₄ Cl at pH of the soils; measurement by AAS (K, Na, Mg, Ca). (Thomas 1982)
<u>Exchangeable Aluminum</u>	Extraction with 1 N KCl, 1 N LaCl ₃ or 1 N CuCl ₂ , measured by AAS-graphite furnace. (Juo and Kamprath 1979; Bloom <i>et al.</i> 1979)
<u>Pyrophosphate Extractable Al</u>	Extraction with 0.1 M sodium pyrophosphate (approximates "organic" fraction). (McKeague <i>et al.</i> 1967; Blume <i>et al.</i> 1986; Cappo <i>et al.</i> 1986)
<u>NH₄-Oxalate Extractable Al</u>	Extraction with 0.2 M NH ₄ -oxalate (subtraction of pyrophosphate extractable fraction approximates amorphous* fraction). (McKeague <i>et al.</i> <i>al.</i> 1971; Blume <i>et al.</i> 1986; Cappo <i>et al.</i> 1986)
<u>Dithionite Extractable</u>	Extraction with citrate-dithionite-bicarbonate (subtraction of NH ₄ -oxalate extractable fraction approximates "crystalline" fraction). (USDA/SCS 1984; Blume <i>et al.</i> 1986; Cappo <i>et al.</i> 1986)

Record analysis results in laboratory notebook
and store instrument printouts in separate folder.



If analytical variation is greater than
established criteria rerun analysis.



Log data in microcomputer file (LOTUS 123) and
check for transcription errors by crosschecking
back to original data forms.



Check for outliers by running range query
checks in LOTUS 123, reanalyze if necessary



Archive data on floppy disks



Transfer data to central data base management
system of Watershed Manipulation Project

Figure C-1-1. Flow Chart of Data Reduction Scheme

APPENDIX C-2

CATION RESUPPLY AND CHEMICAL WEATHERING AT WATERSHED SITES MANIPULATED TO RECEIVE ACIDIC DEPOSITION

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TASK DESCRIPTION

Objective: To determine if several hypotheses about cation resupply and chemical weathering are applicable under laboratory and field conditions.

The following hypotheses relating to model formulation will be tested using laboratory, small plot, and large scale field studies:

1. Ion exchangeable base cations are replenished by chemical weathering.
2. The rate of chemical weathering is a function of the fractional-order hydrogen ion activity in soil solution.
3. The rate of chemical weathering is dependent on the organic ligand concentration in soil solution.
4. The kinetics of chemical weathering in the field can be predicted by laboratory experiments.
5. Silica concentrations in surface water and soil solutions can be used to calculate (on a stoichiometric basis) the amount of chemical weathering of alumino-silicate minerals in the watershed.

Soil samples will be obtained from several horizons at a number of locations in the WMP study area. Studies using a batch pH stat, a fluidized bed reactor, and soil columns will be conducted in the laboratory in which the rate of chemical weathering is measured as a function of simulated acid rain, pH, organic ligand concentration and temperature. Mass balances will be performed on the soil and water samples to measure cation resupply and silica/cation ratios as a function of weathering. Ion budgets will be performed on small and large scale field plots subjected to simulated acid rain. These ion budgets will be used to estimate weathering and cation resupply rates.

ORGANIZATION AND RESPONSIBILITIES

Professor Jerry Schnoor has responsibility of overall task coordination. All work by the University of Wyoming will be overseen by Professor James I. Drever. Column and batch pH-stat studies will be conducted at the University of Iowa. Professor Jerry Schnoor will be in charge of all column studies and Professor Richard Valentine will be in charge of all batch pH studies. Fluidized bed studies will be conducted at the University of Wyoming. The University of Wyoming will also have primary responsibility for conducting all field studies.

All physical-chemical characterization/mineralogy of soil samples will be the responsibility of the University of Wyoming except for grain size measurements which will be conducted by the University of Iowa. The University of Wyoming will also separate soils into fractions which will be studied.

QA/QC activities at the University of Iowa will be the responsibility of the Environmental Engineering Laboratory Director, Dr. Kent Johnson. He will insure that all QA/QC procedures are being followed as described in this document and that data quality objectives are being met. Dr. Norbert Swoboda-Colberg will be in charge of QA/QC activities at the University of Wyoming.

QUALITY ASSURANCE OBJECTIVES

Quality assurance objectives are based on precision and accuracy estimates given in Table C-2-1. Precision and accuracy estimates are given two ways: a percentage value which applies over the levels in which errors are approximately proportional to the machine response (generally at the higher concentrations), and an absolute measurement value which applies as the lower limits of detection are approached. Our precision and accuracy goals are determined by the estimate which results in the largest value of each. Table C-2-4 shows units to be used in correspondence between task groups and with the EPA. Also shown in Table C-2-4 is the estimated range of parameter values.

SAMPLE PROTOCOLS

Soil Samples

Soil samples will be taken (from a number of locations) and several horizons at the WMP site at one time. Sampling of soils to be used in laboratory experiments will be coordinated by the University of Maine in consultation with a field technician from the University of Wyoming.

Field Solutions

Water samples from lysimeters will be collected and analyzed by the University of Maine. A field technician from the task groups will be responsible for installation of lysimeters. Maine will coordinate field measurements.

Lab Samples

Water samples generated during the lab studies will be taken as needed during the experiments. For column and fluidized bed experiments, samples will be taken daily until steady-state is reached. Samples will be taken once or twice daily during the batch pH studies when water composition is to be determined. Acid consumption rate will be determined at least 2-3 times per day in the batch pH stat experiments until the rate of consumption appears constant.

SAMPLE CUSTODY

A summary of storage and special handling procedures is given in Table C-2-3.

Soil Samples

Soil samples will be collected by the site team in plastic bags, and labelled with date, site, and horizon identifiers. All samples will be stored at 4°C. Samples to be used in laboratory studies will be split in the field and one set sent to the University of Iowa and another to the University of Wyoming. Subsamples used in laboratory experiments or for characterization will be dried at 110°C immediately prior to use. Methods developed for the National Acid Deposition Soil Survey will be employed. Soil samples will be stored in the Environmental Engineering Laboratory of the University of Iowa and at the University of Wyoming. Separated soil fractions will be sent from Wyoming to Iowa. These subsamples will be labelled with appropriate identifiers including original sample origin (sample number of unfractionated sample) and a unique code for the specific fraction.

Water Samples

Water samples generated during lab studies will be stored in bottles (either plastic or glass depending on the analysis to be done) labelled with a unique code identifying experiment number, date, and sample time. Sample preservation is by acidification for metals and silica, or by freezing for anions and ammonium if the samples are to be stored for long periods of time. Hydrogen ion is determined immediately upon collection and no storage is required. Water samples will be stored at the Environmental Engineering Laboratory at the University of Iowa and at the University of Wyoming.

Sample Tracking

All samples sent between Maine and Wyoming, Maine and Iowa, or Iowa and Wyoming will be tracked using a sample log book which will note the time of receipt/shipping, the sample descriptor (unique number and 2-3 word descriptor), the person accepting/sending the sample, and place of storage (when received). Each sample will have a label which fully describes the sample as described in sections 5.1 and 5.2.

ANALYTICAL PROCEDURES

Wet chemical analyses will be done in the laboratories at the University of Iowa in Iowa City and the University of Wyoming in Laramie. Table C-2-2 summarizes the types of analyses to be performed and methods to be employed at both locations. The University of Iowa analytical instrumentation consists of an ion chromatograph, an atomic absorption spectrophotometer (AAS), UV-VIS spectrophotometer, and an autotitrator. In addition Iowa is equipped to perform a sieve analysis to obtain grain size distributions.

The University of Wyoming analytical instrumentation consists of two organic carbon analyzers (a coulometric titrator constructed in-house and a commercially available unit, Oceanographic International), an atomic absorption spectrophotometer (AAS), an autotitrator (constructed in-house), an X-ray diffractometer, a BET surface area analyzer, and an inductively coupled plasma spectrophotometer (ICP). In addition, pH meters are available at both locations.

The University of Iowa studies will be conducted in the Environmental Engineering laboratories located at the University of Iowa Water Treatment plant in Iowa City. All University of Iowa instrumentation is also located in the Environmental Engineering labs. University of Wyoming instrumentation is located in room 311 G in the Department of Geology and Geophysics, except the equipment needed to determine surface area which is located in the Wyoming Research Institute. Field lysimeter samples will be analyzed by the University of Maine under their QA/QC procedures.

pH

The pH of laboratory generated water samples will be measured with a digital Beckman model pH 71 or comparable meter. An automatic temperature compensation probe will be used when the instrument has capabilities to use this accessory. Otherwise temperature will be corrected manually.

Cations/Ammonia

Cations will be determined using a Perkin-Elmer Atomic Absorption Spectrophotometer when adequate sample size is available. Na and K will be determined with air-acetylene flame atomic absorption spectrophotometry (AAS). Ca and Mg will be determined by nitrous oxide-acetylene flame AAS. Samples will be aspirated directly into the instrument. Aluminum (total and ion exchangeable

fractions) will be determined using graphite furnace AAS, nitrous oxide-acetylene flame AAS or by ICP. Extractable aluminum will be determined using MIBK extraction. Ten percent of all samples will be run in duplicate. Several experiments will necessitate the taking of relatively small sample volumes (e.g., pH stat experiments) which may make analysis by AAS methods difficult. This will require that Na, K, Ca, and Mg be analyzed by Ion Chromatography. Colorimetry (manual) using a modified phenol-hypochlorite method (Solorzano, 1969) will be used to measure total ammonia when adequate sample size is available. Ion Chromatography will be used when only small sample volumes are available.

DOC

Dissolved organic carbon will be determined by either coulometric titration or by infrared analysis using an Oceanographic International carbon analyzer. All samples will be run in duplicate. Samples will be filtered using a 0.45 silver metal filter.

Anions

Major anions will be determined using a Dionex model 200i Ion Chromatograph at Iowa using $\text{HCO}_3^-/\text{CO}_3^{2-}$ eluant on a type AS-4A column, or by a Dionex model 16 Ion Chromatograph at Wyoming using a type AS-1 column. Ten percent of all samples will be run in duplicate.

Silica

Molybdate reactive silica (by the Molybdosilicate method, APHA, 1980) will be determined colorimetrically (manual method) using either a Baush and Lomb model 70 spectrophotometer or a Perkin-Elmer model 552 High Performance UV-VIS Scanning Spectrophotometer or comparable unit. At least 10% of all silica samples will be run in duplicate.

Surface Area

Surface area will be determined by the BET method. When sufficient sample material is available, 3 samples will be used for each determination.

Alkalinity (Acid Neutralizing Capacity)

Alkalinity will be determined by Gran titration using an automatic titrator (Stumm and Morgan, 1981).

CEC/Extractable Bases

Soil samples will be extracted using NH_4Cl . Major cations (Mg, Ca, K, Na) will be measured using atomic absorption spectrophotometry, ion chromatography or by ICP. Ammonia will be extracted from the soil sample using an HCl rinse and the recovered ammonia determined either by colorimetry (Solorzano, 1969) or by Ion Chromatography.

Soil Bulk Chemistry/Mineralogy

Soil samples/fractions will be dissolved using lithium metaborate fusion. Base cations will be determined using AA or ICP at the University of Wyoming. Mineralogy will be determined using X-ray diffraction. Silica and aluminum will be determined as previously described.

CALIBRATION PROCEDURES

Atomic Absorption Spectrophotometer/ICP

Element standards will be prepared from ACS reagent grade chemicals or from atomic absorption reference standards. The instrument is calibrated before each set of analysis using 3 standards. Standards are rechecked every 10-20 samples and recalibration is performed as needed. A low and high internal standard will be included with each batch of samples.

Ion Chromatography

The instrument will be calibrated with 3-5 standards at the start of each run, and 1-2 standards are run every hour of continuous use. A high and low internal QC standard will be run with each batch to insure integrity of the results and to provide statistical information of precision and accuracy.

UV-VIS Spectrophotometer

The instrument will be calibrated with standards before each batch of analyses, and standard will be included 5-10 samples. A low and high internal QC standard will be run with each batch.

Carbon Analyzer

An organic carbon stock standard will be prepared using potassium dihydrogen phthalate dried at 105°C for two hours. This solution will be stored in an amber bottle at 4°C and used for no longer than one month after preparation. NSW calibration procedures will be used. A high and low DOC internal QC sample will be run with each batch. Every tenth sample will be a DOC standard.

BET Surface Area Analyzer

Manufacturer's recommendations will be followed. One sample will be used as an internal quality control measure and to estimate precision.

pH Meter

Meters will be calibrated with buffers before each set of measurements. Two-point calibration will be used. Additionally, electrode performance in low ionic strength water will be verified by analysis of pH 4.7 standardized acids as specified in the NADP Quality Assurance Report 1979 and in the draft "Sampling and Analysis Protocol for Chemical Characteristics of Lakes and Streams Sensitive to Acidic Deposition", dated May, 1985.

X-ray Diffractometry

Reference minerals will be used to calibrate/standardize the instrument.

PREVENTATIVE MAINTENANCE

Atomic Absorption Spectrophotometer/ICP

The burner heads on the AAS will be routinely cleaned and soaked. The nebulizer, fuel lines, regulators, and gauges are cleaned and adjusted as needed. Spare hollow cathode lamps will be kept on hand. Similar maintenance procedures will be followed for the ICP at Wyoming.

Ion Chromatograph

The Ion Chromatograph columns will be regenerated and replaced as necessary. The conductivity cell will be cleaned and recalibrated every 150 hours of operation.

Carbon Analyzers

The carbon analyzers will be routinely maintained according to the manufacturer's recommendations or the procedures developed at the University of Wyoming.

pH Meter

The pH meter requires no routine maintenance. Spare batteries, chart paper and properly conditioned electrodes will be kept on hand.

INTERNAL QC CHECKS AND CORRECTIVE ACTION

All instruments are maintained and calibrated at least according to the manufacturers specification. Standards are run both before and after running actual samples. Spiked samples will also be run. If significant differences are obtained between the two sets of calibration standards then the samples will be rerun. In addition a low and high concentration internal quality control sample will be run with each batch. The same or similar sample will be used throughout the study. The low/high concentration internal QC samples will be samples that contain known concentrations of each analyte. The solutions will contain either one or several analytes and the same samples will be run throughout the study unless we run out of sample. They will be stored appropriately (see Table C-2-3) and subjected to analysis along with each batch of samples obtained from the lab experiments. These will be prepared using deionized water either from reagent grade chemicals in our lab or from purchased reference standards. The primary purpose is to insure that the instrument is working consistently on a day to day basis. They are not used to calibrate the instrument. In addition, they can be used to estimate precision at the two extremes in concentration. Spiked QC samples will also be run with each analytical batch.

At least 10% of all cation and anions will be measured in duplicate. EPA QC samples for each substance will also be routinely run. Precision and accuracy will be checked each time an analysis is performed. In addition, 10% of all batch pH stat and fluidized bed experiments will be run in duplicate.

Cations by AAS

High and low concentration QC samples are run periodically during analysis of each batch of samples. A series of reagent blanks are run with each batch. Spiked samples are routinely analyzed to verify that there are no matrix effects. With each batch of 20-30 samples, at least one USGS Standard Rock Sample for QC will be included. The standard will vary depending on the composition of the unknown. Samples will be regularly exchanged with the Denver USGS.

Anions/Cations/Ammonia by IC

The IC is standardized before each session and standards periodically run. High and low concentration QC samples are run periodically during analyses of each batch of samples. A series of reagent blanks are run with each batch. Spiked samples are routinely analyzed to assess matrix effects.

DOC

The carbon analyzers are calibrated according to manufactures specification or in-house procedures. Standards, high and low concentration QC samples are run periodically during analysis of each batch of samples. A series of reagent blanks are run with each batch. Spiked samples are routinely analyzed to assess matrix effects.

Silica/Ammonia by Colorimetry

The spectrophotometer is calibrated using standards. In addition, high and low concentration QC samples will be run during analysis of each batch of samples. A series of reagent blanks are also run. Spiked samples will be routinely used to assess matrix effects.

Surface Area

The manufacturer's recommendations will be followed. In addition, one soil sample will be used as an internal QC check by periodically determining its surface area.

Alkalinity (Acid Neutralizing Capacity)

Standard solutions will be periodically titrated.

Weathering Rates

10% of all pH stat experiments and fluidized bed experiments will be run in duplicate in order to estimate precision in measuring weathering rates.

CEC/Extractable Bases

One sample will be periodically used as an internal QC sample unless it becomes necessary to use another sample.

Mineralogy

Internal QC checks include frequent checking of the goniometer calibration by the positions and sharpness of quartz peaks. Most samples contain quartz which serves as an internal standard. In addition, the laboratory has standard quartz and silicon mounts and a chlorite standard for checking low-angle peaks. Cross-comparison for identification criteria will be performed by using American Petroleum Institute clay mineral standards. QC samples will also be exchanged with the Western Research Institute and with the Wyoming Geological Survey. Both of these laboratories have modern X-ray diffraction systems and extensive experience.

PERFORMANCE AND SYSTEM AUDITS

The WMP Performance Audit Program will provide blind audit samples from EMSL-LV on a quarterly frequency for the following parameters to both the University of Wyoming (Drever) and the University of Iowa (Schnoor and Valentine): ANC, anions, base cations, DOC, NH_4 , pH, and Si. In addition, the University of Iowa lab will receive audit samples for total-Al. The University of Wyoming will participate in the Forest Response Program (FRP) Soil Sample Exchange Program for the following parameters: base cations, CEC, exchangeable acidity, and pH.

System audits will be conducted in cooperation with EPA at least annually.

DATA REDUCTION, VALIDATION, AND REPORTING

Data Reduction Scheme

Cations by AAS/ICP --

The atomic absorption spectrophotometer and ICP are calibrated with appropriate standards. Signal output from all standards will be recorded and periodic checks manually made to insure accuracy and linearity.

Anions/Cations/Ammonia by IC --

The Dionex Ion Chromatograph at the University of Iowa is connected to a model 4270 Dionex data capture device. The ion chromatograph at the University of Wyoming is connected to a Varian model 401 data capture device. Peak areas are logged and automatically converted to concentrations. A graphical output is also produced so that any anomalous looking peaks can be flagged.

DOC --

A recording integrator determines carbon content based on comparisons with known standards.

pH --

pH is read directly from the meter.

Silica/Ammonia by Colorimetry --

Silica and ammonia concentration is determined manually from a calibration curve.

Surface Area --

Determined from the amount of nitrogen gas sorbed to the sample.

Alkalinity (Acid Neutralizing Capacity) --

Determined by Gran titration with acid using an automatic titrator.

Data Validation and Treatment of Outliers

Data transfer is minimized to minimize transfer error. Data is originally recorded in laboratory notebooks. At each transfer step, the data are rechecked for transfer error. Data values will be tested for outlier status as described in Designation D 2777, Annual Book of ASTM Standards, Part 31-91977. If the value is rejected the sample will be reanalyzed. If replicate analyses deviate by more than the known precision of the analysis, the analysis will be repeated.

REPORTING OF QUALITY ASSURANCE

Summaries of duplicate analyses, spiked samples, performance audits, and other QC checks will be included with each quarterly report to the EPA Project Officer. The annual report will include a compilation and interpretation of the quarterly QA reports.

TABLE C-2-1. ANALYTICAL PROCEDURES AND QUALITY ASSURANCE OBJECTIVES

Parameter	Method	Reference Conditions	Precision ^{1,3}	Accuracy ^{2,3}
pH	Electrode	NADP QA Report (1979)	± 3%	± 7%
DOC	a) Infrared Analyzer b) Coulmetric titrator		±10%, ± 0.1 ppm as C	+10%, ± 0.1 ppm as C
Na,K, Ca,Mg	a) Flame AA b) ICP c) Ion Chromatography	EPA-600/4-79-020 Perkin-Elmer, 1981 Thermal Jarrel-Ash Dionex Stnd. Methods	±10%, ±10 µeq/l ±10%, ±10 µeq/l ±10%, ±10 µeq/l	±10%, ±10 µeq/l ±10%, ±10 µeq/l ±10%, ±10 µeq/l
Total Al	a) Graphite Furnace AA b) ICP	Hillman <i>et al.</i> , 1986 Thermal Jarrel-Ash	±25%, ±40 ppb as Al ±25%, ±40 ppb as Al	±30%, ±40 ppb as Al ±30%, ±40 ppb as Al
Ammonia	a) Ion Chromatography b) Colorimetry (modified) phenol-hypochlorite method)	a) Dionex Stnd. Mtds. b) Solarzano, 1969	±10%, ±10 µeq/l ±10%, ±10 µeq/l	±10%, ±10 µeq/l +10%, ±10 µeq/l
SO ₄ ²⁻ , Cl NO ₃ ⁻	Ion Chromatography	Dionex Stnd. Methods	±10%, ±10 µeq/l	±10%, ±10 µeq/l
Silica	a) Colorimetry (Molybdosilicate method) b) ICP	APHA, 1980 Thermal Jarrel-Ash	±10%, ±200 ppb as Si ±10%, ±200 ppb as Si	±10%, ±200 ppb as Si ±10%, ±200 ppb as Si
Alkalinity	Gran Titration	Stumm and Morgan, 1981	±5%, ±10 µeq/l	±7%, ±10 µeq/l
Surface Area	BET analysis	Manufacturer's manual		±20%±30%
CEC	NH ₄ Cl extraction with ammonia analysis	Modified from Acid Deposition Soil Survey	±20%	--
Extractable Bases	NH ₄ Cl extraction analysis by AA/ICP	Modified from Acid Deposition Soil Survey	±20%	--
Weathering Rate	Acid consumption rate/dissolution rate	--	± 20%	--
Grain Size	Sieve analysis	USGS	±10% by wt.	--

¹ Precision = 100 s/xm where s is the sample standard deviation and xm is the sample mean.

² Accuracy = 100 (xm-T)/T where T is the "true" or reference value.

³ The range of the absolute measurement value applies for precision and accuracy as the lower limits of detection are approached.

TABLE C-2-2. SUMMARY OF METHODS/LOCATION OF ANALYSES

Analysis	Method by Location	
	Iowa	Wyoming
SOIL EXTRACTS		
Base Cations	AA/IC	AA/ICP
Aluminum	AA (with/wo extraction)	AA/ICP
Anions	Ion Chromatography (IC)	Ion Chromatography
Ammonia	IC/Phenolhypochlorite	IC
pH	Electrode	Electrode
Alkalinity	Gran titration	Gran Titration
Silica	Colorimetry	Colorimetry, ICP
DOC Soils	—	Infrared analyzer/coulometric titrator
Bulk chemistry metaborate	—	AA/ICP after HF dissolution or lithium fusion
Mineralogy	—	X-ray Diffraction
CEC/extractable bases	—	Unbuffered NH_4Cl method
Exchangeable Acidity	—	KCl method (according to Methods Manual for the National Acid Deposition Soil Survey)
Grain size distribution	Sieve analysis (USGS methods)	—
Surface area	—	BET

TABLE C-2-3. SUMMARY OF STORAGE/SPECIAL HANDLING

Parameter	Analytical Method	Preservation Method/ Special Procedures
pH	Electrode	Samples processed immediately
Dissolved Organic Carbon (DOC)	Infrared Analyzer/ Coulometric Titrator	Filter thru baked silver metal membrane (0.45 μ Selas)
Na, K, Ca, Mg	Atomic Absorption/ Ion Chromatography/ICP in LPE bottles (APHA, 1980)	Filter thru 0.45 μ , acidify to pH $\leq$ 4*, store at room temp.
Total Al	Atomic Absorption/ICP, w/wo MIBK extraction, AA flame/graphite	Filter thru 0.45 μ , acidify to pH $\leq$ 2*, store at 4°C in LPE bottles (APHA, 1980)
Ammonia	Ion Chromatography/ Colorimetry (modified phenol-hypochlorite method, Solarzano)	Filter thru 0.45 μ , freeze in LPE storage bottle
SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , F ⁻	Ion Chromatography in LPE bottles (APHA, 1980)	Filter thru 0.45 μ , store at 4°C
Total Silica	Colorimetry (Molybdsilicate method)/ ICP	Filter thru 0.45 μ , acidify to pH $\leq$ 2*, store at room temp. in LPE storage bottles, (APHA, 1980)
Alkalinity	Gran Titration polyethylene bottle	Store at 4°C in amber
Surface Area	BET analysis	Manufacturer's procedure
CEC	Unbuffered NH ₄ Cl extractions. Ammonia analysis	Manual extractions
Extractable Bases	NH ₄ Cl extraction/AA/ICP	Manual extractions

* Acidification with HNO₃

TABLE C-2-4. REPORTING UNITS AND APPROXIMATE RANGES OF PARAMETERS

Parameter	Units	Range
pH	pH	1-7
DOC	ppm as C	0.1-100
Na,K, Ca,Mg	$\mu\text{eq/l}$	10-1000
Total Al	ppb as Al	40-2000
Ammonia	$\mu\text{eq/l}$	10-1000
SO ₄ , Cl, NO ₃	$\mu\text{eq/l}$	10-1000
Silica	$\mu\text{moles/l}$	10-500
ANC	$\mu\text{eq/l}$	$\pm 10-1000$
Surface area	m ² /gram	0.2-200
CEC	meq/kg	10-1000
Extractable Bases	meq/kg	10-1000
*Weathering rate	meq/kg/d picomoles/m ² /sec	--
Grain size	% by wt.	--

* Method - (Acid consumption rate/dissolution rate)

APPENDIX C-3

NITRATE MOBILITY AND NITROGEN CYCLING

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TASK DESCRIPTION

Research Objective: To evaluate the effects of sulfur and nitrogen additions in the acid deposition context on nitrogen mineralization and nitrification in soils, nitrate mobility and leaching, net primary productivity and nutrient allocation in vegetation, and foliage litter decay within forested watershed ecosystems.

This task will involve measurements of several processes important in nitrogen cycling in two types of experimental settings.

In the whole watershed treatments, nitrogen mineralization and nitrification will be measured in soils in the two Bear Brook catchments using an on-site incubation technique at 20 random sampling points within each of the 10 plots to be established in each catchment. This method (described below) is repeated monthly and yields measurements of net nitrogen mineralization and nitrification for soils incubated under field conditions. Monthly values are summed for annual totals. Measurements of nitrate and ammonium leaching from soils will be carried out on the watershed-level treatments by other task groups.

In the experimental plots outside the manipulated catchments the effects of higher dosages of nitrogen and sulfur, alone and in combination, will be measured. Separate sets of three replicate plots (15m by 15m each) will be established for controls and additions of 3000 and 6000 eq/ha/yr of sulfate, 3000 and 10,000 eq/ha/yr of nitrate, and 3000 eq/ha/yr of both nitrate and sulfate.

In all of the experimental plots we will measure nitrogen mineralization and nitrification using the on-site technique. In the nitrogen-only and nitrogen-plus-sulfur plots, we will also measure the total biomass of foliage and fine roots and its nitrogen content, total net primary productivity, and decomposition rates of foliage of dominant species in the watershed. Leaching losses of nitrate and ammonium from these plots will be measured by the site team.

Relatively few types of analytical procedures are required to fulfill this research plan, although large numbers of samples will be generated. The measurements of ammonium and nitrate required for the mineralization, nitrification and nitrogen content of biomass values will be carried out on the Technicon TRAACS system. The TRAACS system is a more highly automated version of the Technicon AutoAnalyzer II system which has become a standard device for measuring nitrate and ammonium at the concentrations encountered and the ionic strengths and pH values present in the solutions used to extract or digest samples.

ORGANIZATION AND RESPONSIBILITIES

J. Aber (New Hampshire) will be responsible for all the mineralization and fine root samples. K. Nadelhoffer (Ecosystems Center) will be responsible for tree biomass measurements, litterfall measurements and litter decay studies (in addition to plot maintenance). Mineralization and nitrification laboratory analyses will be performed at the University of New Hampshire in John Aber's laboratory.

QUALITY ASSURANCE OBJECTIVES

It is not possible to fully document the analytical errors for the new Technicon TRAACS system as we have had no experience with it. The AutoAnalyzer II system has been very reliable. Technicon lists accuracy and precision statistics for the nitrate and ammonium analyses at <1% of sample value for

moderate concentrations levels. The soil extracts and tissue digestates we commonly analyze have relatively high concentrations (range of 0 to 10 ppm N as nitrate or ammonium) and replicate analyses of test solutions show this 1% figure to be accurate. We assume that performance characteristics will be better on the TRAACS system. However, based on comparisons between runs, and on samples cross-checked from other laboratories which involves other sources of error, we can guarantee only less than 10% precision and 5% accuracy on these samples.

To test these performance characteristics, and to document variation introduced by sampling and extraction procedures, we propose first a pilot study of the nitrogen mineralization and nitrification method adjacent to the treatment plots outside the experimental watersheds. Twenty replicate soil cores will be incubated in each of two soil horizons. A paired initial sample will be collected for each incubated sample. These initial samples will be well mixed. Half of each sample will then be composited with half portions of three other initial samples. Four subsamples from both the original 20 and 5 composited samples will be analyzed for extractable nitrate and ammonium content (see below for description of analytical procedure). Incubated samples will be collected after one month in the field and divided into separate and composite samples as described for initials.

For both initial and incubated samples, soils will be well mixed and four subsamples will be taken. Each subsample will be analyzed for extractable ammonium and nitrate. Four subsamples will be taken from each extractant solution for analysis of nitrate and ammonium concentration. Extracted soils will be filtered and dried so that comparisons can be made on a dry weight soil basis. The precision of each step in this procedure (sampling, extraction, analysis) will be determined as standard deviation and coefficient of variation. In addition, the effect of the compositing procedure described in the proposal and field implementation plan on total sampling error will be assessed for the soils at the Bear Brook site. We anticipate that sampling variation will overwhelm analytical error due to the heterogeneous nature of soils and soil organic matter. We have performed informal internal audits of sampling versus analytical variation. Sampling variation is on the order of 15% in these analyses, while analytical error is generally around 1%. These values are sufficient for testing the hypotheses contained in the proposal.

A similar procedure will be followed for analyses of total nitrogen content of tissues. Again, informal internal audits show that sample variation is much greater than analytical variation.

Because we will use newly purchased equipment for all our chemical analyses, we will conduct a lengthy and thorough series of trials to establish the accuracy of our methods, and to develop manuals of standard operating procedures. However, because of our previous experience with very similar devices, the relatively high ratio of sampling to analytical variation and the relatively high concentrations of nitrogen compounds in the solutions to be analyzed, we anticipate no problem in meeting our requirements.

SAMPLE PROTOCOLS

Sampling will be carried out as described in the Field Implementation Plan.

Nitrogen Mineralization and Nitrification on Soils

Initial and incubated soil samples for the nitrogen mineralization procedure will generally be placed in the KCl extract immediately after collection and compositing in the field and always within 1 day of collection. 100 ml of the 1N KCl solution is placed into previously rinsed plastic containers (capped and disposable) and carried into the field. Soil samples are collected, composited and an amount approximately equal to 10g dry weight is deposited into each jar. Extractant is removed from the jars

between 24 and 48 hours after collection. Scintillation vials with extractant solution will be kept on ice until reaching the lab in Durham, NH, where they will be frozen until analyzed. Extraction time cannot be more than 48 hours as enzymatic breakdown within the soil sample is not inhibited, and may actually be increased by the high ionic strength solution used. Extractant solution is decanted into washed and rinsed plastic scintillation vials and frozen until analyzed. We have stored frozen samples for up to six months. However, the large sample throughput required for this project will assure that the TRAACS system will be in operation most of the time and thus frozen solution storage time should be minimal.

Total Tissue Nitrogen

Samples for total tissue nitrogen concentration will be collected in paper bags and air dried immediately and further dried at 70°C when they arrive at the lab. Total nitrogen content of air dried leaves is very stable. The 70°C temperature is selected to avoid volatilization of nitrogen compounds. Dried samples are ground in a UDY Mill, redried and analyzed for total nitrogen content using a modified Kjeldahl (Caro's acid) method developed for the block digester and TRAACS system. Ten grams of sample are added to 25 ml of sulfuric acid in a block digester tube and allowed to react for 10 minutes in the pre-heated block. The tubes are then removed and 5 ml of hydrogen peroxide (50%) is added to each. After the peroxide reaction has subsided, the tubes are replaced in the block and the heating, cooling and peroxide additions are repeated twice more. The samples are then digested for an additional 30 minutes before cooling and dilution to 100 ml for analysis. Ammonium concentrations in the digestate are measured by color development at 660 nm resulting from the reaction of ammonia, sodium salicylate, sodium nitroprusside and sodium hypochlorite in a buffered alkaline medium at a pH of 12.8-13.0.

Biomass and Productivity Samples

Collection of biomass and productivity samples is very straightforward. In deciduous forests, such as the northern hardwood stands which dominate the Lead Mountain site, foliar biomass can be estimated by collection of leaf litter fall. This is done using seven 0.5 by 0.5 meter traps per plot. This will give a standard error of the mean of less than 15% of the mean for total foliage biomass. Material in traps is collected monthly throughout the snow-free period, except for weekly collections during periods of heavy litter fall in autumn. Collected material is air-dried immediately and then oven-dried (70°C) for final weight determination and for total nitrogen analyses.

Measuring total fine (<3mm diameter) root biomass is time consuming as it involves hand sorting of roots from the surrounding soil matrix, but is otherwise not difficult to achieve. We will collect and sort 10 fine root samples per plot in both the forest floor and top 10cm of the mineral soil. Samples are held under refrigeration in plastic bags until they can be sorted. Fine roots lose weight very slowly when refrigerated, and can be held for up to three months before sorting. Stem and branch biomass can be estimated by allometric relationships using stem diameter as the measured variable. Stem production is estimated by measuring annual change in stem diameter and using allometric equations to predict current and previous stem biomass. We will carry out a 100% sample on tree diameters within each plot. Nitrogen content of all collected materials is determined by modified Kjeldahl digestion procedures followed by analysis of digestate on the TRAACS system.

Foliage decomposition samples are handled in much the same way. Retrieved nylon mesh bags with decaying litter enclosed are first oven dried (70°C) to reduce further microbial activity. Tissues are then removed from the bags, weighed and ground for storage until total nitrogen contents can be determined using the modified Kjeldahl procedure described above.

SAMPLE CUSTODY

The procedures described here vary widely in the potential for errors due to contamination or modification of samples. Least sensitive are the tissue samples for total nitrogen content. These can be air dried and then oven dried and kept for long periods before analysis. They will be dried, weighed and ground in Woods Hole, and then transported to Durham, NH for nitrogen analyses.

Soil samples used for mineralization and nitrification measurements can be held for up to two days without serious effect before extraction. However, we have devised a simple system for carrying the KCl solution into the field so that incubations can begin immediately following the compositing of samples. Extractant solutions can be kept frozen for up to six months. Samples are labelled with plot name, sample type, and date. A field notebook is used to record samples collected, and a lab notebook is used as a sample log book.

ANALYTICAL PROCEDURES

The Technicon TRAACS system uses the same chemistries as the Autoanalyzer II. Ammonium is measured by color development at 630 nm caused by the reaction of an ammonium salt with sodium phenoxide followed by the addition of sodium hypochlorite (the Berthelot reaction). Nitrate is first reduced to nitrite using a cadmium reductor column and then measured by color development at 550 nm caused by the reaction of nitrite with sulfanilamide under acidic conditions to form a diazo compound, which further reacts with N-1-Naphthylethylenediamine dihydrochloride. Technicon has also developed a hydrazine method for measuring nitrate concentrations which removes the requirement for the nitrate reductor column, but we have not had the opportunity to evaluate this procedure, but is part of the standard analytical procedures for the TRAACS system and has received EPA approval.

Total tissue nitrogen content is determined using a modified Kjeldahl (Caro's acid) method developed for the block digester and TRAACS system.

CALIBRATION PROCEDURES

As described above, the Technicon TRAACS system will be the major piece of equipment used in this research project. Nitrate and Ammonium standards will be prepared fresh each day from a stock solution prepared once per month. Initial calibration is with four standards. Standards are rerun once every tray (every 120 samples). Calibration blanks are included with each tray. A system of sample retention for cross-calibration of runs from different times using different reagents and standard solutions will be developed and included in the standard operating procedures. This will include freezing of both standards and samples for cross-calibration through time.

PREVENTATIVE MAINTENANCE

System maintenance will be performed on the Technicon AutoAnalyzer as recommended by the manufacturer, and a log book of actual maintenance performed will be kept.

INTERNAL QC CHECKS AND CORRECTIVE ACTION

To evaluate analytical precision on a continuing basis, triplicate analyses will be performed on at least one percent of each of the types of analyses described in this proposal. We will also carry out a system of cross-time calibrations on the TRAACS system as mentioned above. A subsample of these solutions will be kept for cross-checking of the consistency of the TRAACS system between runs.

Matrix spike samples are analyzed for organic soils with highly colored extractant solutions. Reagent blanks are collected for 5% of extractions.

PERFORMANCE AND SYSTEM AUDITS

The WMP Performance Audit Program will provide blind audit samples from EMSL-LV on a quarterly frequency for NH_4 and NO_3 . Soil samples from the Soil Sample Exchange Programs (Section 5 of the Integrated QA Plan) will be analyzed for total nitrogen.

System audits will be conducted in cooperation with EPA at least annually.

DATA REDUCTION, VALIDATION, AND REPORTING

The TRAACS system comes with an IBM PC for data logging, conversion through dilution and sample weight factors, and report writing. A software system is included in the TRAACS package which handles process control as well as data management. The package includes dBASE II for formatting reports. We propose to make the fullest use of this system for standardizing and scheduling data handling and reporting. Hard copies of summarized data on monthly mineralization rates and tissue nitrogen content will be made available to all investigators. Raw data will be stored on floppy disks for archival purposes.

Data on biomass and productivity of foliage, fine roots and woody tissues will be entered into this same system to convert nitrogen concentration data to total amounts.

We have two software packages available for data analysis on microcomputers, Minitab and Statistix (University of Minnesota).

REPORTING OF QUALITY ASSURANCE

Quarterly reports to EPA project officer will include results of QC sample analyses and additional information as required by the EPA (Section 7.0, Integrated QA Plan).

APPENDIX C-4

ROLE OF ORGANIC ACIDS IN AFFECTING SOIL SOLUTION AND SURFACE WATER ACIDIFICATION IN RESPONSE TO WATERSHED MANIPULATIONS

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TASK DESCRIPTION

The Organic Acids Task Group will characterize the Bear Brook catchments for dissolved organic carbon (DOC) fractions in throughfall, soil solutions, and surface waters before, during, and after acidification by sulfuric acid. Laboratory and plot studies will be conducted to examine specific DOC release and retention mechanisms in each watershed. DOC data will be integrated with site and other task area information (e.g., aluminum, sulfur, nitrogen, hydrology, and base cations) to fully understand the effects of acidification on carbon cycling and the resulting influence on surface water acidification.

This research will involve chemical measurements on both solutions and soil samples. We will receive subsamples of solutions (throughfall, soil leachate, and stream) from Bear Brook. We will focus on DOC fractionation of solution samples characterized at the site. Only during laboratory manipulations (column studies) will we analyze for additional parameters. Chemical parameters to be measured and techniques of analysis for these soil column manipulations are listed in Table C-4-1. DOC fractionation and isolation techniques are illustrated in Figures C-4-1 and C-4-2. All DOC fractionations will be conducted at the University of Illinois.

Soil samples will be collected at the Bear Brook catchment and subsamples forwarded to us. Because most National Acid Deposition Soil Survey measurements will be made on the samples, we will only analyze for the carbon fractions listed in Table C-4-1.

ORGANIZATION AND RESPONSIBILITIES

Dr. Mark B. David, the Principal Investigator of the project, will have overall responsibility for project measurements, sample custody, and data reporting. His Quality Assurance responsibilities include:

- Monitoring daily QA/QC activities,
- Reviewing laboratory notebooks, instrument performance logs, and QA/QC data on a regular basis,
- Determining that performance audits, triplicate analyses and other QA/QC activities are performed,
- Examining data summaries and calculations,
- Assisting in trouble-shooting problems,
- Preparing quarterly QA summaries and reports,
- Checking that all project personnel are competent to perform analyses, and
- Ensuring that all Watershed Manipulation Project overall QA/QC operations are followed.

Laboratory chemists, technicians, and graduate research assistants have the responsibility to:

- Understand their role in the project and laboratory,
- Maintain appropriate notebooks, instrument logs, and QA/QC records,
- Observe and record events that may affect experimental data,

- Report any problems or concerns to the principal investigator, and
- Perform routine maintenance on instrumentation as required.

Regular meetings of project personnel will be held to discuss experimental progress, analytical problems or concerns, or any other problems within the project.

QUALITY ASSURANCE OBJECTIVES

Quality assurance objectives for subsamples analyzed at the University of Illinois are listed in Tables C-4-1 and C-4-2. Quality assurance objectives for samples analyzed at the University of Maine are listed in Table 9 in the main text of the Integrated QA Plan.

SAMPLE PROTOCOLS

Acid washing procedure is 15-10 minutes (longer for new containers) in 1N HCl or HNO₃, then rinse with distilled water. Containers for DOC samples and cleaning procedures are still being determined.

Solution subsamples from Bear Brook catchments and external plots (throughfall, gravity and tension lysimeter, stream water) will be provided by the University of Maine. Protocols will be determined during initial laboratory work.

Soil samples will be collected at two year intervals on both control and manipulated catchments, as well as external plots. Protocols will be coordinated through overall project management.

Solution samples from laboratory manipulations will be collected weekly during each experiment from the bottom of each soil column. All samples will be collected in prelabelled, acid-washed, amber glass containers with teflon lids.

SAMPLE CUSTODY AND PRESERVATION

Solution samples from Bear Brook will be labeled with a unique code identifying type, site, and date of collection. We will obtain subsamples uniquely labeled from each plot. Samples will be stored in amber glass DOC bottles with teflon lids and either acidified to pH 2.0 or stored at 3°C. During initial work on the project we will conduct extensive experiments to determine the best way of transporting and preserving solutions for DOC fractionations. We will work with the University of Maine to insure that these preservation techniques are followed.

Uniquely labeled dried and sieved soil samples will be obtained from Bear Brook for all soil analysis. Samples will be stored at 4°C in 2-liter polyethylene aliquot bottles.

Solution samples from laboratory manipulations at the University of Illinois will be uniquely labeled (experiment, soil column, type of sample, date of sample) and processed immediately. Sample preservation will be by acidification (metals, HNO₃ to pH < 2) or storage at 3°C (anions, DOC fractions, NH₄⁺). Other parameters will be determined on the day of collection, and no storage is required.

ANALYTICAL PROCEDURES

Tables C-4-1 and C-4-2 list all analyses along with referenced standard techniques used at the University of Illinois. Most are similar to the National Surface Water Survey techniques listed by Hillman *et al.* (1986). A book outlining standard procedures will be maintained in the laboratory for reference by all professional and technical personnel. All personnel will be thoroughly trained in proper laboratory procedures before they engage in any experimental analyses. A listing of each technique that will be used in University of Illinois laboratories will be forwarded to EPA. As the work is initiated any modifications to these techniques will be incorporated into these procedures.

CALIBRATION PROCEDURES AND FREQUENCY

Standards and Initial Calibrations

Element standards are prepared in our laboratory from ACS reagent grade chemicals or from atomic absorption reference standards. An initial calibration is performed as necessary for each particular analytical method. The linear dynamic range (LDR) for the initial calibration will be determined. Linearity by least squares will be at least 0.99. The calibration standards will bracket the expected sample concentrations. Samples will be analyzed within the linear dynamic range. If during an analysis the concentration of a sample falls above the LDR, one of two options will be used. One, the sample will be diluted (diluent will have a similar matrix to the sample matrix with respect to any preservative) and reanalyzed. Alternatively, two concentration ranges will be calibrated. Samples will be first analyzed on the lower range. Any samples whose concentration exceeds the upper end of the LDR will then be analyzed on the higher concentration range. If the second option is used, a calibration QC sample will be analyzed for each range.

Atomic Absorption Spectrophotometer

The instrument is calibrated before analysis (5 standards) of each set of samples for each element. QC standards are run every 10 samples and recalibration is performed if needed.

Ion Chromatography

The instrument is calibrated with 4-7 standards at the start of each run, and QC standards are run every ten samples.

Carbon Analyzer

Standard curves will be developed daily utilizing potassium hydrogen phthalate as a primary standard.

pH Meter

Meter will be calibrated with pH 7.0 and 4.01 buffers before each set of measurements. Additionally, electrode performance in low ionic strength water will be verified daily by analysis of pH 4.7 standardized acid.

Specific Conductance Meter

Meter will be calibrated daily with standard KCl solution.

Autotitrator

Standard acid solutions will be run twice a day to verify the instrument response.

PREVENTATIVE MAINTENANCE

We will follow all manufacturers recommendations for each instrument. Routine maintenance procedures will be listed with the operating procedures for each instrument. A log book used for each instrument or procedure will be used to determine numbers of samples between various maintenance procedures and when the procedures are due. Preventative maintenance procedures will be periodically updated if necessary to reflect operating requirements of the laboratory. Spare parts kits will be maintained for each instrument.

INTERNAL QC CHECKS AND CORRECTIVE ACTION

Internal quality control checks will follow the protocols used for the National Acid Deposition Soil Survey as much as possible. These checks are discussed below in the manner in which they will be used for this project.

Sample Collection and Preparation

Duplicate Sample Analysis --

Five percent of the samples will be prepared and analyzed in duplicate. The coefficient of variation (CV) between duplicates will be calculated for an estimate of precision. The values will be plotted on a control chart and 99% and 95% confidence intervals established (control and warning limits, respectively). Initial control limits are set at the levels given in Table C-4-4. The control limits should not exceed these values. If duplicate values fall outside the values in the tables, an explanation will be sought (such as instrument malfunction, calibration drift, etc.). A second, different sample must then be analyzed in duplicate. No further samples will be analyzed until duplicate sample results are within the control limits.

$$CV = \frac{S}{x} \times 100$$

Reagent Blank --

A reagent blank will be prepared and analyzed for methods which require extractions. A reagent blank will be a sample composed of all the reagents (in the same quantities) used in preparing a real sample for analysis. It will undergo the same processing as a real sample. The concentration of the reagent blank must be less than the required detection limit. If the concentration exceeds this, the source of contamination will be found and eliminated. A new reagent blank will be prepared, analyzed, and the same criteria applied. All samples associated with the "high" reagent blank will be reanalyzed when the contamination is eliminated.

Sample Analysis

Calibration QC Sample --

The calibration QC sample will be a known sample containing the analyte of interest at a concentration in the mid-calibration range. It will be obtained commercially or prepared by the analyst from source which is independent of the calibration standards. The calibration QC sample will be analyzed prior to any samples, and after every 10 samples, and after the last sample. The observed value for the QC sample will be checked to see that it does not differ from the theoretical value by more than the limits in Table C-4-4. When an unacceptable value for the calibration QC sample is obtained, then the instrument will be recalibrated. All samples up to the last acceptable QC sample will also be reanalyzed.

Detection Limit QC Sample --

The detection limit QC sample will be a known sample containing the analyte of interest at a concentration 2-3 times the required detection limit. A detection limit QC sample will be analyzed once every 40 samples. The measured value of the detection limit QC sample must be within 20% of the theoretical value. If not, the problem will be identified, corrected, and an acceptable result obtained prior to sample analysis.

Blank Analysis --

Once per 40 samples a calibration blank will be analyzed. The calibration blank is defined as "0" mg/L standard and contains only the matrix of the calibration standards. The observed concentration of the calibration blank must be less than twice the instrument detection limit. If not, the instrument will be zeroed and the calibration rechecked.

Matrix Spike Analysis --

One matrix spike will be prepared for every 20 samples. A matrix spike will be prepared by spiking an aliquot of a sample with a known quantity of analyte. The spike concentration will be the larger of twice the endogenous level or 10 times the required detection limit. Also, the volume of the spike added will be negligible (less than or equal to 1/1000 of the sample aliquot volume). The percent recovery of the spike is calculated as follows:

$$\% \text{ spike recovery} = \frac{\text{Value of sample plus spike} - \text{value of unspiked sample}}{(\text{value of spike added})} \times 100$$

The spike recovery will be 100 ± 15 percent. If the recovery is not within this range, two additional, different samples will be spiked, analyzed, and recoveries calculated. If one or both recoveries are not 100 ± 15 percent, the samples will be analyzed by standard additions. The standard addition will be performed by analyzing the sample, sample plus a spike at about the endogenous level, and sample plus a spike at about twice the endogenous level.

Conductivity Balance

The specific conductance of each sample will be estimated by summing the equivalent conductances (at infinite dilution) for each measured ion. The equivalent conductance for each ion will be estimated by

multiplying the ion concentration by the appropriate factor in Table C-4-5. The percent conductance difference (%CD) will be calculated as follows:

$$\% \text{ Conductance difference} = \frac{\text{Calculated cond.} - \text{measured cond.}}{\text{measured conductance}} \times 100$$

This balance will be useful for stream solutions with low DOC. However, for soil solutions it may not be very useful.

PERFORMANCE AND SYSTEM AUDITS

Performance audit samples from EPA and the National Bureau of Standards will be used at least every other month throughout the duration of the project. No performance samples are available for the DOC fractionation techniques that will be used in this project. Only total DOC can be evaluated. The WMP Performance Audit Program will provide blind audit samples from EMSL-LV on a quarterly frequency for the following parameters: total Al, Al fractions, ANC, anions, base cations, DOC, Fe, NH_4 , pH, and sp. cond. Soil samples from the Forest Response Program (FRP) Soil Sample Exchange Program and the EMSL-LV Soils Exchange Program will be analyzed for total organic C.

System audits will be conducted in cooperation with EPA at least annually.

DATA REDUCTION, VALIDATION, AND REPORTING

Data Reduction

Solution Cations –

The atomic absorption spectrophotometer is calibrated with appropriate standards (4-7 standards) spanning the linear range of suspected unknowns and concentration is read directly from the instrument and recorded.

Solution Anions –

Peak areas are integrated and concentrations calculated by a Dionex 4270 integrator.

Specific Conductance, pH, ANC –

Specific conductance and pH are read directly from the meters and recorded in μS at 25°C and pH units, respectively. ANC is calculated from the titration curve of the autotitrator using the proper Gran function.

DOC –

A reporting integrator determines carbon concentration based on comparisons with known standards.

DOC Fractions –

After each fraction is separated the carbon concentration is determined and reported as in 8.4.

Data Verification

All initial data results will be recorded in ink in bound laboratory notebooks, dated, and signed by the personnel making the measurements. Printouts or data summaries from various instruments will be stapled to appropriate pages in the notebooks. The next transfer step will be to Lotus or similar software files on a microcomputer. After this transfer printouts of the data are checked manually for transcription errors. All data will be entered twice into this system, uploaded to SAS files on an IBM 4341 mainframe, and compared using SAS data comparison programs. If files are not identical checks will be made to find the differences and correct them by verifying against original data sheets.

Data Validation and Treatment of Outliers

Data will be examined through descriptive SAS procedures such as univariate to check for outliers. If a value is rejected the sample will be reanalyzed if possible. Where possible (solutions with low DOC), cation-anion charge balances will be used to check solution values along with calculated versus measured specific conductance.

Data Reporting Scheme for Laboratory Data

See Figure C-4-3.

Data Management for Overall Project

We will be one part of the Watershed Manipulation Project. We will incorporate our data into the overall project data base as discussed in the research plan. Through this central data management system we will have access to both our data along with other task and site information. This scheme is outlined in Figure C-4-4.

REPORTING OF QUALITY ASSURANCE

Summaries of duplicate analysis, spiked samples, performance audits, and other QA checks will be included with each quarterly report to the Project Officer at EPA. A separate section in each quarterly report will be entitled "Quality Assurance Results - Date of Quarter." The annual report will include a compilation and interpretation of the quarterly QA reports.

TABLE C-4-1. ANALYTICAL TECHNIQUES FOR SOLUTION SAMPLES AND QUALITY ASSURANCE OBJECTIVES.

Parameter	Technique	Precision	Accuracy
Acid neutralizing capacity	Titration with Gran plot	± 5%	± 7%
Aluminum, total	EPA Method 202.2 AAS - furnace	± 10%	± 20%
Aluminum, total extractable	Extraction with 8-hydroxyquinoline into MIBK followed by AAS - furnace	± 10%	± 20%
Ammonium, dissolved	Steam distillation (Keeney and Nelson, 1982)	± 15%	± 10%
Calcium, dissolved	EPA Method 215.1 AAS - flame	± 5%	± 5%
Chloride, dissolved	Ion chromatography	± 5%	± 5%
Fluoride, total	Ion selective electrode	± 10%	± 10%
Iron, dissolved	EPA Method 236.1 AAS - furnace	± 10%	± 10%
Magnesium, dissolved	EPA Method 242.1 AAS - flame	± 5%	± 5%
Nitrate,	Ion chromatography	± 5%	± 5%
Organic carbon, dissolved	EPA Method 415.2	± 5%	± 10%
Organic carbon fractionation, dissolved	Leenheer (1985)	± 20%	-
pH	glass electrode and meter	± 5%	± 5%
Potassium, dissolved	EPA Method 258.1 AAS - flame	± 10%	± 10%
Sodium, dissolved	EPA Method 273.1 AAS - flame	± 5%	± 5%
Specific conductance	EPA Method 120.1	± 5%	± 10%
Sulfate, dissolved	Ion chromatography	± 5%	± 5%

TABLE C-4-2. ANALYTICAL TECHNIQUES FOR SOIL SAMPLES AND QUALITY ASSURANCE OBJECTIVES.

Parameter	Technique	Precision	Accuracy
Total carbon	LECO total C analyzer	± 10%	± 10%
Humic & fulvic acid content	Schnitzer (1982)	± 20%	N/A
Humic material characterization	Schnitzer (1982)	N/A	N/A
a. Functional group analyses - total acidity - CO₂H groups - acidic OH groups b. Infrared spectrometry c. HA/FA ratio d. E₄/E₆ ratio e. Elemental analyses			

TABLE C-4-3. QA OBJECTIVES AND REPORTING UNITS

Parameter	Reporting Unit	Reporting Format	Expected Range	Lower Reporting Limit
Organic carbon, dissolved	mg L ⁻¹	+0.01 units	0-100	0.2 mg L ⁻¹
Organic carbon fractionation, dissolved	mg L ⁻¹	+0.01 units	0-20	0.2 mg L ⁻¹
Total organic carbon, soil	% dry wt	+0.1%	0-50%	0.2%

Parameter	Lower Range	Precision at Lower Range	Upper Range	Precision at Upper Range
Organic carbon, dissolved	0.2-1	20%	2-100	10%
Organic carbon fractionation, dissolved	0.2-1	20%	2-20	20%
Total organic carbon, soil	0.2-1	20%	2-50	10%

TABLE C-4-4. MAXIMUM CONTROL LIMITS FOR QC SAMPLES

Parameter	Maximum Control Limit for QC Sample (% Deviation from Theoretical Concentration of QC Sample)
ANC	$\pm 5\%$
Aluminum, total	$\pm 20\%$
Aluminum, total extractable	$\pm 20\%$
Ammonium	$\pm 10\%$
Calcium	$\pm 5\%$
Chloride	$\pm 5\%$
Fluoride	$\pm 10\%$
Iron	$\pm 10\%$
Magnesium	$\pm 5\%$
Nitrate	$\pm 5\%$
Organic carbon, dissolved	$\pm 10\%$
pH	$\pm 5\%$
Potassium	$\pm 10\%$
Sodium	$\pm 5\%$
Specific conductance	$\pm 10\%$
Sulfate	$\pm 5\%$

TABLE C-4-5. CONDUCTANCE FACTORS OF IONS. FROM APHA ET AL (1985) AND WEAST (1972)

Ion	Specific Conductance ($\mu S/cm$ at 25°C) per mg/L	Ion	Specific Conductance ($\mu S/cm$ at 25°C) per mg/L
Ca^{2+}	2.60	Na^+	2.13
Cl^-	2.14	NH_4^+	4.13
CO_3^{2-}	2.62	SO_4^{2-}	1.54
H^+	3.5×10^5 (per mole/L)	NO_3^-	1.15
HCO_3^-	0.715	K^+	1.84
Mg^{2+}	3.62	OH^-	1.92×10^5 (per mole/L)

$$[H^+] \text{ moles/L} = 10^{-pH}$$

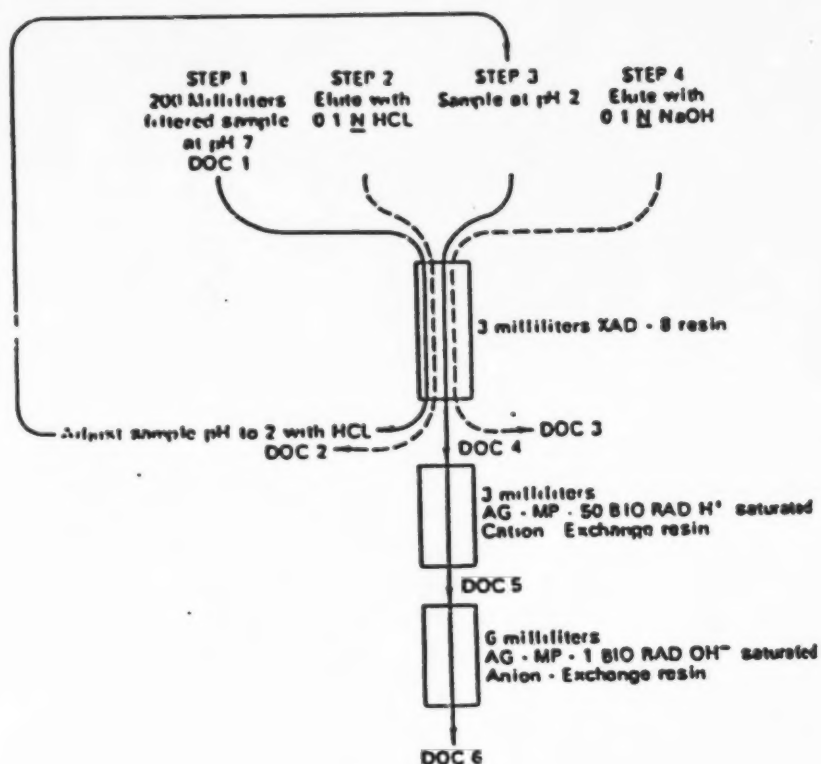
pH = pH determined at V=0 of the acidity titration

$$[OH] = \frac{K_W}{[H^+]}$$

$$HCO_3^- = \frac{5.080 [DIC(mg/L)] [H^+] K_1}{[H^+]^2 + [H^+] + K_1 K_2}$$

$$CO_3^{2-} = \frac{4.996 [DIC(mg/L)] K_1 K_2}{[H^+]^2 [H^+] K_1 + K_1 K_2}$$

$$K_1 = 4.3 \times 10^{-7} \quad K_2 = 5.61 \times 10^{-11}$$



CALCULATIONS

Hydrophobic DOC (mg/L)			
Total	DOC 1	DOC 4	
Bases	DOC 2	$\times \frac{\text{elute volume}}{\text{sample volume}}$	
Acids	DOC 3	$\times \frac{\text{elute volume}}{\text{sample volume}}$	
Neutrals	Total	Bases + Acids	

Hydrophilic DOC (mg/L)	
Total	DOC 4
Bases	DOC 4 + DOC 5
Acids	DOC 5 + DOC 6
Neutrals	DOC 6

Figure C-4-1. Analytical scheme for dissolved organic carbon fractionation (From Leenheer, 1985).

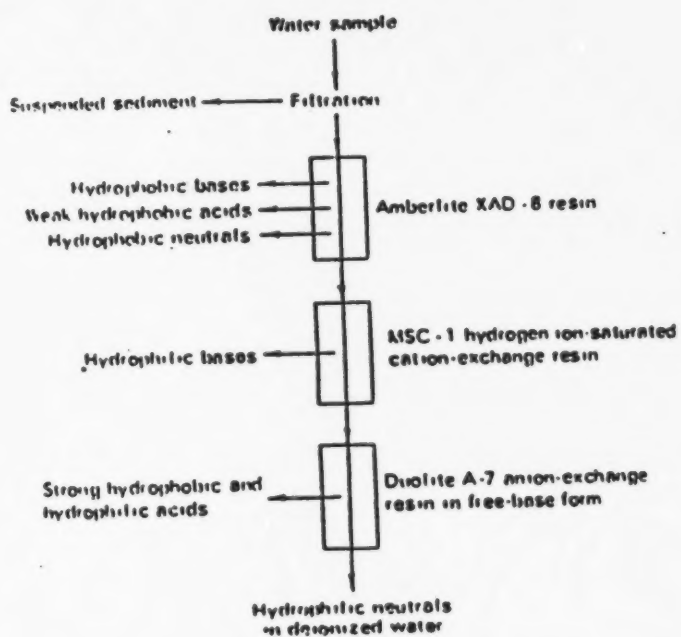


Figure C-4-2. Preparative scheme for dissolved organic carbon fractionation (from Leenheer, 1985).

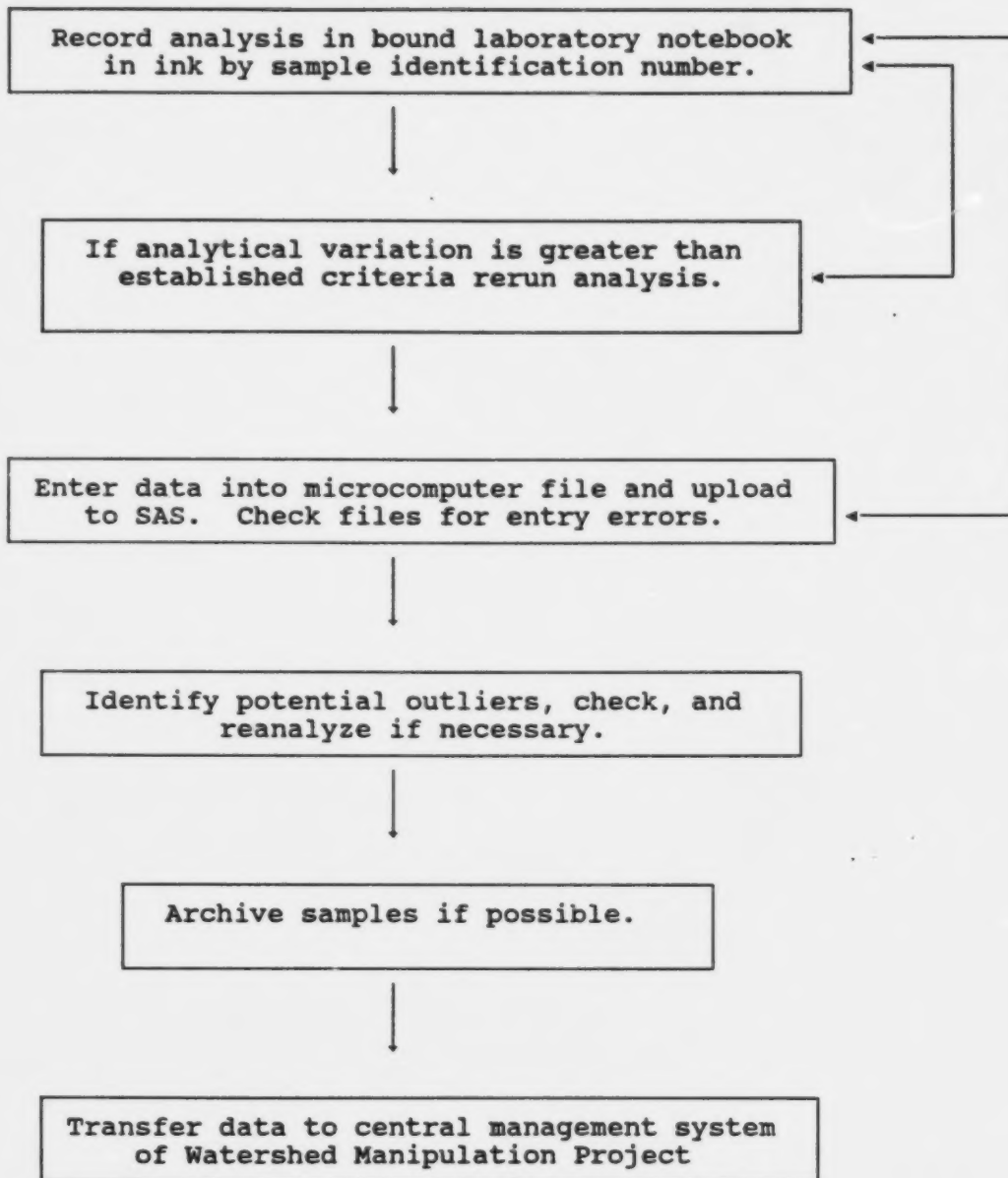


Figure C-4-3. Data reporting scheme.

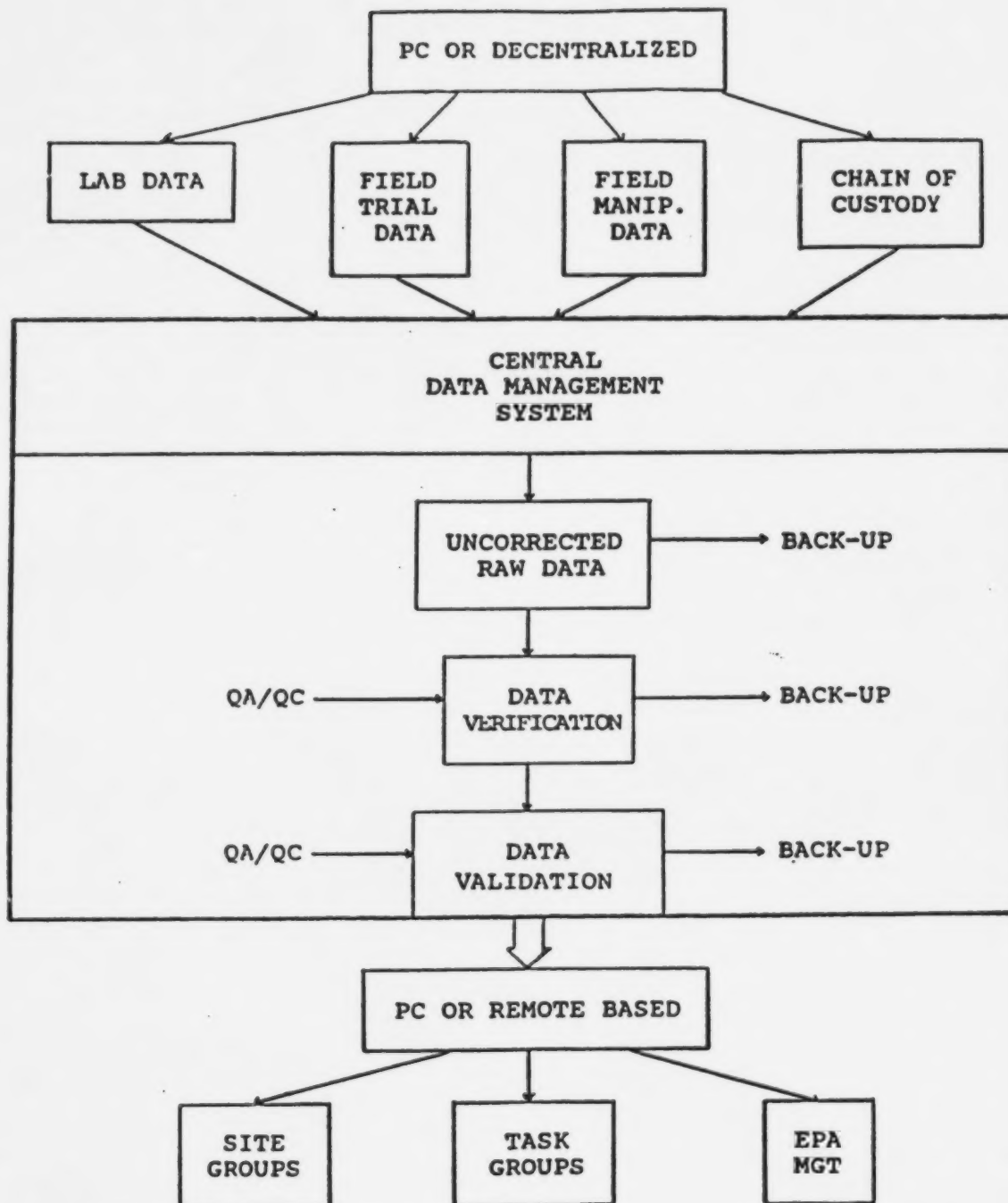


Figure C-4-4. Watershed Manipulation Project data management procedures.

APPENDIX C-5

CONTROLS ON SULFUR BUDGETS AND SULFATE MOBILITY FOR WATERSHED MANIPULATION PROJECT

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TASK DESCRIPTION

This project is part of the Watershed Manipulation Project's research effort conducted at the Bear Brook Site in Maine. The Site will be characterized for organic and inorganic sulfur fractions in soil, vegetation, and solutions before, during, and after experimental acidification. Laboratory and plot studies will be conducted to examine specific sulfur retention mechanisms and sulfur dynamics in each watershed. Radioactive and stable sulfur isotopes will be used in both laboratory and plot level manipulations to evaluate sulfur dynamics and sulfur cycling in each watershed. Sulfur data will be integrated with site and other task area information (e.g. aluminum, organic acids, nitrogen, hydrology, and base cations) to fully understand the effects of acidification on sulfur cycling and the resulting influence on surface water acidification.

Research will involve chemical measurements on solutions, soil and vegetation samples. We will receive subsamples of solutions (throughfall, soil leachate, and stream) from the Bear Brook site. These samples will be analyzed for most constituents determined in the National Surface Water and National Acid Deposition Soil Surveys. Actual parameters and techniques can be found in individual Site and Task Quality Assurance Plans. We will focus on sulfur fractionation of samples characterized by each site. Only during laboratory manipulations (column and absorption studies) will we analyze for additional parameters. Chemical parameters to be measured and techniques of analysis for these laboratory manipulations are listed in Table C-5-1. Also selected solution samples will be analyzed for total sulfur as described in Landers et al. (1983).

Soil samples will be collected by each site and subsamples forwarded to us. Because most National Acid Deposition Soil Survey measurements will be made on the samples, we will only analyze for the sulfur fractions listed in Table C-5-2. Vegetation subsamples will also be forwarded in a similar manner and will be analyzed for the sulfur fractions listed in Table C-5-2.

ORGANIZATION AND RESPONSIBILITIES

Dr. Myron J. Mitchell, the Principal Investigator of the project, will have overall responsibility for project measurements, sample custody, and data reporting. Dr. Mitchell's lab at Syracuse will be responsible for all sample preparation and sample tracking among the labs in this task.

Because measurements will be made at several different laboratories, each of the co-principal investigators will have responsibility for Quality Assurance for measurements made at their laboratories. Quality Assurance responsibilities for the principal and co-principal investigators include:

- Monitoring daily QA/QC activities,
- Reviewing laboratory notebooks, instrument performance logs, and QA/QC data on a regular basis,
- Determining that performance audits, triplicate analyses and other QA/QC activities are performed,
- Examining data summaries and calculations,
- Assisting in trouble-shooting problems,
- Preparing quarterly QA summaries and reports,

- Checking that all project personnel are competent to perform analyses, and
- Ensuring that all Watershed Manipulation Project overall QA/QC operations are followed.

Dr. Mitchell will have the additional responsibility of coordinating work among the investigators and ensuring similar Quality Assurance procedures are carried out.

Laboratory chemists, technicians, and graduate research assistants have the responsibility to:

- Understand their role in the project and laboratory,
- Maintain appropriate notebooks, instrument logs, and QA/QC records,
- Observe and record events that may affect experimental data,
- Report any problems or concerns to the principal investigator, and
- Perform routine maintenance on instrumentation as required.

Regular meetings of project personnel at each laboratory will be held to discuss experimental progress, analytical problems or concerns, or any other problems within the project. Telephone calls and regular meetings will be held among the principal investigator and co-principal investigators to discuss the above issues as well.

QUALITY ASSURANCE OBJECTIVES

Quality assurance objectives for samples analyzed within the Sulfur Task Area are listed in Tables C-5-1 and C-5-2.

SAMPLE PROTOCOLS

Solution samples from each manipulation site (throughfall, gravity and tension lysimeter, stream water) will be provided by each site. Protocols will be set by each site and coordinated through overall project management.

Soil and vegetation samples will be provided by each site at two year intervals on both control and manipulated sites. Protocols will be set by each site and coordinated through overall project management. Additional soil samples from plot level manipulations will be collected in a similar manner as the catchment scale sites.

Solution samples from laboratory manipulations will be collected weekly during each experiment from the bottom of each soil column. All samples will be collected in prelabelled, acid-washed, polyethylene containers.

SAMPLE CUSTODY

Solution samples from each site will be labeled with a unique code identifying type, site, and date of collection. We will obtain subsamples uniquely labeled from each site.

Field moist soil samples will be obtained as subsamples from each site during catchment and plot soil sampling. Samples will be frozen at each site and shipped to Dr. Mitchell's laboratory at Syracuse. Each sample will be freeze-dried and stored in a polyethylene bottle for analysis. Freeze-drying will be used to avoid alterations in S constituents from air or oven drying. During initial work we will conduct extensive checks between field moist and freeze dried samples to ensure that changes in S constituents or other soil fractions have not occurred.

Solution samples from laboratory manipulations will be uniquely labeled (experiment, soil column, type of sample, date of sample) and processed immediately. Sample preservation will be by storage at 3°C for anions and acidification to pH 2 for metals. Other parameters will be determined on the day of collection, and no storage is required.

ANALYTICAL PROCEDURES

A book outlining standard procedures will be maintained in the laboratory for reference by all professional and technical personnel. All personnel will be thoroughly trained in proper laboratory procedures before they engage in any experimental analyses. Table C-5-1 and C-5-2 list all analyses along with referenced standard techniques. Most are similar to the National Surface Water Survey techniques listed by Hillman *et al.* (1986) and National Acid Deposition Soil Survey techniques listed by Blume *et al.* (1986).

CALIBRATION PROCEDURES

Initial Calibration

Element standards are prepared in our laboratory from ACS reagent grade chemicals or from atomic absorption reference standards. An initial calibration will be performed as necessary for each particular analytical method. The linear dynamic range (LDR) for the initial calibration will be determined. Linearity by least squares will be at least 0.99. The calibration standards will bracket the expected sample concentrations. Samples will be analyzed within the linear dynamic range. If during an analysis the concentration of a sample falls above the LDR, one of two options will be used. One, the sample will be diluted (diluent will have a similar matrix to the sample matrix with respect to any preservative) and reanalyzed. Alternatively, two concentration ranges will be calibrated. Samples will be first analyzed on the lower range. Any samples whose concentration exceeds the upper end of the LDR will then be analyzed on the higher concentration range. If the second option is used, a calibration QC sample will be analyzed for each range.

Atomic Absorption Spectrophotometer

The instrument is calibrated before analysis of each set of samples for each element. QC standards are run every 10 samples and recalibration is performed if needed.

Ion Chromatography

The instrument is calibrated with 4-7 standards at the start of each run, and QC standards are run every ten samples.

pH Meter

Meter will be calibrated with pH 6.86 and 4.01 buffers before each set of measurements. Additionally, electrode performance in low ionic strength water will be verified daily by analysis of pH 4.7 standardized acid. Buffers are run every ten samples and recalibration is performed if necessary.

Specific Conductance Meter

Meter will be calibrated daily with standard KCl solution.

Carbon Analyzer

Standard curves will be developed daily utilizing sodium carbonate primary standards.

PREVENTIVE MAINTENANCE

For all instruments used in this project, a permanent bound notebook is kept which records the number and types of analyses. If when running standards it is found that the standard curves or specifications have deviated greater than the known precision of the instrument, the cause of this deviation is ascertained. If it is established that there is a mechanical or electrical problem which cannot be fixed by the operator necessary, an instrument specialist is brought in to examine the source of the problem. The College of Environmental Science and Forestry provides a technical service section to help in these procedures. If the problem cannot be rectified by College personnel, outside expertise is utilized.

The liquid scintillation counter is under a service contract with Beckman and yearly its counting efficiency is ascertained. Also all glassware used in the sulfur fractionation procedure is examined before use and if found defective due to cracks or other damage, the glass blower at the College of Environmental Science and Forestry either repairs the damage or a replacement part is fabricated. All other instruments in the laboratory follow the normal routine maintenance procedures indicated in their respective manuals.

INTERNAL QC CHECKS AND CORRECTIVE ACTION

Internal quality control checks will follow the protocols used for the National Acid Deposition Soil Survey as much as possible. These checks are discussed below in the manner in which they will be used for this project for analyzing ion chromatography and AAS procedures. In addition, all Johnson-Nishita procedure S analyses are routinely conducted in triplicate and calibrated daily against NBS standards.

Sample Collection and Preparation

Duplicate Sample Analysis --

Five percent of the samples will be prepared and analyzed in duplicate. The coefficient of variation (CV) between duplicates will be calculated. The values will be plotted on a control chart and 99% and 95% confidence intervals established (control and warning limits, respectively). Initial control limits are set at the levels given in Tables C-5-1 and C-5-3. The control limits should not exceed these values. If duplicate values fall outside the values in the tables, an explanation will be sought (such as instrument malfunction, calibration drift, etc.). A second, different sample must then be analyzed in

duplicate. No further samples will be analyzed until duplicate sample results are within the control limits.

$$CV = \frac{S}{\bar{x}} \times 100\%$$

Reagent Blank --

A reagent blank will be prepared and analyzed for methods which require extractions. A reagent blank will be a sample composed of all the reagents (in the same quantities) used in preparing a real sample for analysis. It will undergo the same processing as a real sample. The concentration of the reagent blank must be less than the required detection limit. If the concentration exceeds this, the source of contamination will be found and eliminated. A new reagent blank will be prepared, analyzed, and the same criteria applied. All samples associated with the "high" reagent blank will be reanalyzed when the contamination is eliminated.

Sample Analysis

Calibration QC Sample --

The calibration QC sample will be a known sample containing the analyte of interest at a concentration in the mid-calibration range. It will be obtained commercially or prepared by the analyst from source which is independent of the calibration standards. The calibration QC sample will be analyzed prior to any samples, after every 10 samples, and after the last sample. The observed value for the QC sample will be checked to see that it does not differ from the theoretical value by more than the limits in Table C-5-3. When an unacceptable value for the calibration QC sample is obtained, then the instrument will be recalibrated. All samples up to the last acceptable QC sample will also be reanalyzed.

Detection Limit QC Sample --

The detection limit QC sample will be a known sample containing the analyte of interest at a concentration 2-3 times the required detection limit. A detection limit QC sample will be analyzed once every 40 samples. The measured value of the detection limit QC sample must be within 20% of the theoretical value. If not, the problem will be identified, corrected, and an acceptable result obtained prior to sample analysis.

Blank Analysis --

Once per 40 samples a calibration blank will be analyzed. The calibration blank is defined as "0" mg/L standard and contains only the matrix of the calibration standards. The observed concentration of the calibration blank must be less than twice the instrument detection limit. If not, the instrument will be zeroed and the calibration rechecked.

Matrix Spike Analysis --

One matrix spike will be prepared for every 20 samples. A matrix spike will be prepared by spiking an aliquot of a sample with a known quantity of analyte. The spike concentration will be the larger of twice the endogenous level or 10 times the required detection limit. Also, the volume of the spike added will be negligible (less than or equal to 1/1000 of the sample aliquot volume).

The percent recovery of the spike is calculated as follows:

$$\% \text{ spike recovery} = \frac{\text{Value of sample plus spike} - \text{Value of unspiked sample}}{(\text{value of spike added})} \times 100$$

The spike recovery will be 100 ± 15 percent. If the recovery is not within this range, two additional, different samples will be spiked, analyzed, and recoveries calculated. If one or both recoveries are not 100 ± 15 percent, the samples will be analyzed by standard additions. The standard addition will be performed by analyzing the sample, sample plus a spike at about the endogenous level, and sample plus a spike at about twice the endogenous level.

Conductivity Balance

The specific conductance of each sample will be estimated by summing the equivalent conductances (at infinite dilution) for each measured ion. The equivalent conductance for each ion will be estimated by multiplying the ion concentration by the appropriate factor in Table C-5-4. The percent conductance difference (%CD) will be calculated as follows:

$$\% \text{ Conductance difference} = \frac{\text{Calculated cond.} - \text{measured cond.}}{\text{measured conductance}} \times 100\%$$

This balance will be useful for stream solutions with low DOC. However, for soil solutions it may not be very useful.

Radioactive S Analysis

Internal standards will be used to account for differences in counting efficiencies. Internal standards are also checked against ^{14}C certified standards to determine absolute instrument counting efficiency.

Stable S Isotopes

The Micromass 602 analyzer has been calibrated against the standard Canyon Diablo troilite meteorite. Samples of a light $+1.2 \Delta^{34}\text{S}$ (pyrite ore) and heavy $+19.5 \Delta^{34}\text{S}$ (AgS) internal laboratory standard are run daily in the Stable Isotope Laboratory at the University of Calgary.

PERFORMANCE AND SYSTEM AUDITS

Performance audit samples from EPA and National Bureau of Standards will be used at least bi-monthly throughout the duration of the project. The WMP Performance Audit Program will provide blind audit samples from EMSL-LV on a quarterly frequency for the following parameters: total Al, ANC, anions, cations, DOC, Fe, NH_4 , pH, and special conditions. Soil samples from the Soil Sample Exchange Programs (Section 5 of the Integrated QA Plan) will be analyzed for total S and S-fractions.

System audits will be conducted in cooperation with EPA at least annually.

DATA REDUCTION, VERIFICATION, VALIDATION, AND REPORTING

Data Reduction

Solution Cations --

The atomic absorption spectrophotometer is calibrated with appropriate standards (4-7) spanning the range of unknowns and concentration is read directly from the instrument and recorded directly into computer files.

Solution Anions --

Peak areas are integrated and concentrations calculated by an IBM-PC linked to the ion chromatograph with an analog to digital converter with user designed software.

Specific Conductance, pH, ANC --

Specific conductance and pH are read directly from the meters and recorded in uS at 25°C and pH standard units, respectively. ANC is calculated from the titration curve of the autotitrator using the proper Gran function.

DOC --

A reporting integrator determines carbon concentration based on comparisons with known standards.

Sulfur Constituents --

Standard curves are generated daily using a stock solution for intra-laboratory determinations. Curves are compared among days and if a curve deviates from previous curves the procedure is repeated and the problem which resulted in the deviation ascertained if possible. Sample S contents are calculated from the daily standard curve.

Data Verification

All initial data results will be recorded in ink in bound laboratory notebooks, dated, and signed by the personnel making the measurements. Printouts or data summaries from various instruments will be stapled to appropriate pages in the notebooks. The next transfer step will be to Lotus or similar software files on a microcomputer. After this transfer printouts of the data are checked for transcription errors. All data will be entered into this system and uploaded to SAS files on an IBM 3700 mainframe or microcomputer version of SAS.

Data Validation and Treatment of Outliers

Data will be examined through descriptive SAS procedures such as univariate to check for outliers. If a value is rejected the sample will be reanalyzed if possible. Where possible (solutions with low DOC), cation-anion charge balances will be used to check solution values along with calculated versus measured specific conductance.

Data Reporting Scheme for Laboratory Data

See Figure C-5-1.

Data Management for Overall Project

We will be one part of the Watershed Manipulation Project. We will incorporate our data into the overall project data base as discussed in the research plan. Through this central data management system we will have access to both our data along with other task and site information. This scheme is outlined in Figure C-5-2.

REPORTING OF QUALITY ASSURANCE

Summaries of triplicate analysis, spiked samples, performance audits, and other QA checks will be included with each quarterly report to the Project Officer at EPA. A separate section in each quarterly report will be entitled "Quality Assurance Results - Date of Quarter." The annual report will include a compilation and interpretation of the quarterly QA reports.

TABLE C-5-1. ANALYTICAL TECHNIQUES FOR SOLUTION SAMPLES AND QUALITY ASSURANCE OBJECTIVES.

Parameter	Technique	Precision	Accuracy
Acid neutralizing capacity	Titration with Gran plot	$\pm 5\%$	$\pm 10\%$
Aluminum, total	EPA Method 202.2 AAS - furnace	$\pm 20\%$	$\pm 20\%$
Calcium, dissolved	EPA Method 215.1 AAS - flame	$\pm 5\%$	$\pm 5\%$
Chloride, dissolved	Ion chromatography	$\pm 5\%$	$\pm 5\%$
Iron, dissolved	EPA Method 236.1 AAS - furnace	$\pm 10\%$	$\pm 10\%$
Magnesium, dissolved	EPA Method 242.1 AAS - flame	$\pm 5\%$	$\pm 5\%$
Nitrate,	Ion chromatography	$\pm 5\%$	$\pm 5\%$
Organic carbon, dissolved	EPA Method 415.2	$\pm 5\%$	$\pm 10\%$
pH	glass electrode and meter	$\pm 5\%$	$\pm 5\%$
Potassium, dissolved	EPA Method 258.1 AAS - flame	$\pm 10\%$	$\pm 10\%$
Sodium, dissolved	EPA Method 273.1 AAS - flame	$\pm 5\%$	$\pm 5\%$
Specific conductance	EPA Method 120.1	$\pm 5\%$	$\pm 10\%$
Sulfate, dissolved	Ion chromatography	$\pm 5\%$	$\pm 5\%$

TABLE C-5-2. ANALYTICAL TECHNIQUES FOR SOIL AND VEGETATION SAMPLES AND QUALITY ASSURANCE OBJECTIVES.

Parameter	Technique	Precision	Accuracy
<u>Soil</u>			
S constituents			
Water extractable sulfate	Ion chromatography	$\pm 10\%$	N/A
Phosphate extractable sulfate	Ion chromatography	$\pm 10\%$	N/A
Total S	Landers <i>et al.</i> (1983)	$\pm 10\%$	$\pm 5\%$
C-bonded S	"	$\pm 10\%$	N/A
Ester sulfate	"	$\pm 10\%$	N/A
Non-sulfate inorganic S	"	$\pm 10\%$	N/A
^{35}S	"	$\pm 10\%$	N/A
Stable S isotopes	Fuller <i>et al.</i> (1986)	$\pm 0.5\text{‰}^{34}\text{S}$	N/A
Sulfate adsorption isotherms	Ion chromatography	$\pm 10\%$	N/A
<u>Vegetation</u>			
Total S	Landers <i>et al.</i> (1983)	$\pm 10\%$	$\pm 10\%$
Sulfate	"	$\pm 10\%$	N/A

TABLE C-5-3. MAXIMUM CONTROL LIMITS FOR QC SAMPLES.

Parameter	Maximum Control Limit for QC Sample (% Deviation from Theoretical Concentration of QC Sample)
ANC	$\pm 5\%$
Aluminum, total	$\pm 20\%$
Calcium	$\pm 5\%$
Chloride	$\pm 5\%$
Iron	$\pm 10\%$
Magnesium	$\pm 5\%$
Nitrate	$\pm 5\%$
Organic carbon, dissolved	$\pm 10\%$
pH	$\pm 5\%$
Potassium	$\pm 10\%$
Sodium	$\pm 5\%$
Specific conductance	$\pm 10\%$
Sulfate	$\pm 5\%$
Sulfur	$\pm 5\%$

TABLE C-5-4. CONDUCTANCE FACTORS OF IONS. FROM APHA ET AL. (1985)
AND WEAST (1972).

Ion	Specific Conductance ($\mu\text{S}/\text{cm}$ at 25°C) per mg/L	Ion	Specific Conductance ($\mu\text{S}/\text{cm}$ at 25°C) per mg/L
Ca^{2+}	2.60	Na^+	2.13
Cl^-	2.14	NH_4^+	4.13
CO_3^{2-}	2.62	SO_4^{2-}	1.54
H^+	3.5×10^5 (per mole/L)	NO_3^-	1.15
HCO_3^-	0.715	K^+	1.84
Mg^{2+}	3.62	OH^-	1.92×10^5 (per mole/L)

$$[\text{H}^+] \text{ moles/L} = 10^{-\text{pH}}$$

pH = pH determined at V=O of the acidity titration

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

$$\text{HCO}_3^- = \frac{5.080 [\text{DIC}(\text{mg/L})] [\text{H}^+] K_1}{[\text{H}^+]^2 + [\text{H}^+] + K_1 K_2}$$

$$\text{CO}_3^{2-} = \frac{4.996 [\text{DIC}(\text{mg/L})] K_1 K_2}{[\text{H}^+]^2 + [\text{H}^+] K_1 + K_1 K_2}$$

$$K_1 = 4.3 \times 10^{-7} \quad K_2 = 5.61 \times 10^{-11}$$

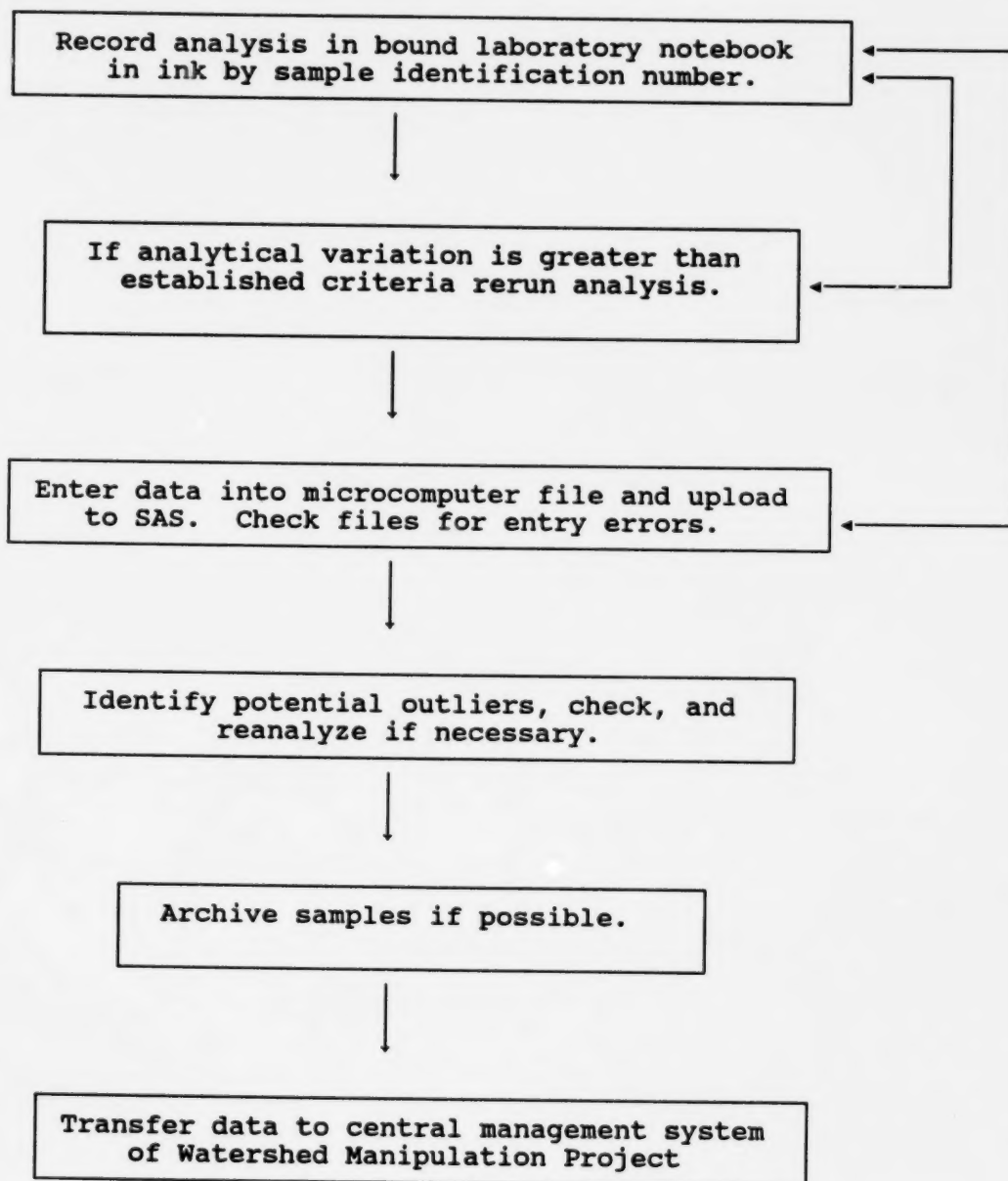


Figure C-5-1. Data Reporting Scheme

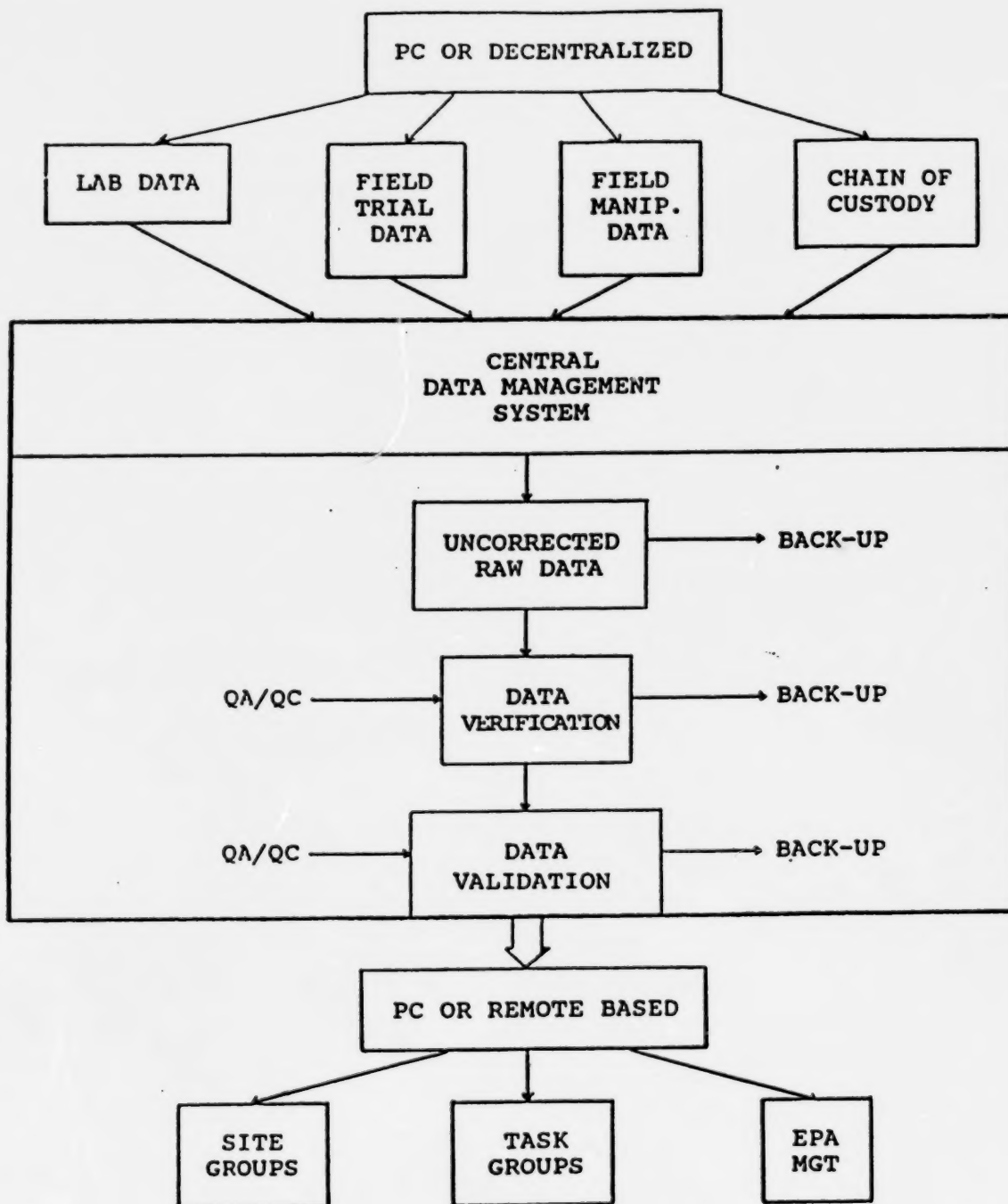


Figure C-5-2. WMP Data Management Procedures